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Catalytic, Interrupted Formal Homo-Nazarov Cyclization with (Hetero)arenes: Access to α-(Hetero)aryl Cyclohexanones

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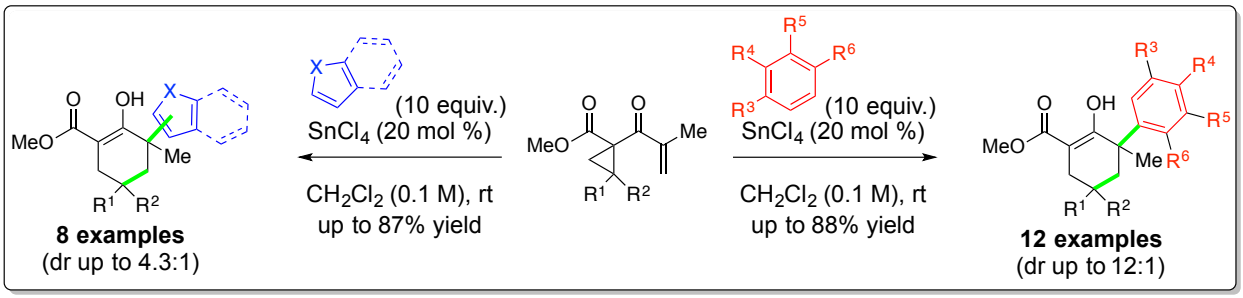
Abstract

The first examples of a Lewis-acid catalyzed (hetero)arene interrupted, formal homo-Nazarov cyclization have been disclosed. Using $SnCl_4$ as the catalyst, alkenyl cyclopropyl ketones undergo ring-opening cyclization to form six-membered cyclic oxyallyl cations. Subsequent intermolecular Friedel-Crafts-type arylation with various electron-rich arenes and heteroarenes provides functionalized α-(hetero)arylated cyclohexanones, a scaffold present in many natural products and bioactive compounds, in yields up to 88% and diastereomeric ratios up to 11.7:1. Regiospecific arylation occurs at the α-carbon of the oxyallyl cation due to polarization caused by the ester group.



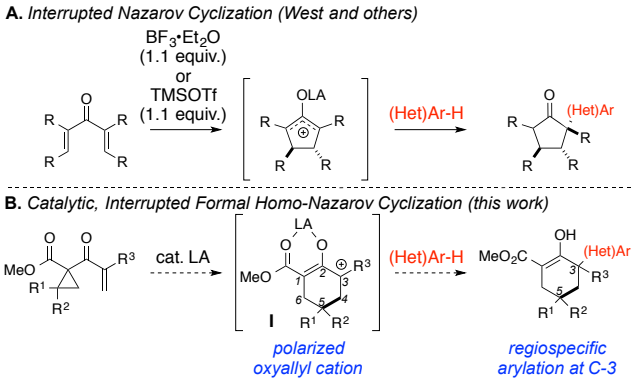
INTRODUCTION

Functionalized α-aryl and heteroaryl cyclohexanones represent two structural frameworks that are present at the core of a number of natural products and pharmaceutical agents.[1] Given their prevalence and importance, various approaches toward α-(hetero)aryl cyclohexanones have been explored by synthetic chemists. Two common approaches involve the direct α-arylation of cyclohexanones via transition metal catalyzed enol(ate) arylation[2] or enolate trapping with diaryl iodonium salts.[3] Both of these approaches utilize aryl and/or heteroaryl halides as electrophilic coupling partners for the enolates. Alternatively, an increasingly popular approach to α-(hetero)aryl cyclohexanones involves the (hetero)arene as the nucleophile and an *in situ*-generated oxyallyl cation[4] as the electrophilic coupling partner in an umpolung fashion (via a Friedel-Crafts-type reaction). For instance, Chi[5] and MacMillan[6] demonstrated that base (Na_2CO_3 or NEt_3) promoted the reaction of indoles with α-halo- or α-tosyloxycyclohexanones to form α-indolylcyclohexanones. Later, Tang reported the reaction of α-chlorocyclohexanone with 2-naphthol.[7] Finally, Kartika reported that 6-membered aryl-substituted α-hydroxy methylenol ethers were readily converted to the corresponding oxyallyl cations and regioselectively trapped by indoles.[8] While each method is powerful in its own right, the classes of arenes employed

(indoles/naphthols) were limited, and the number of actual examples involving cyclohexanones was small (<6 examples). Thus, the broader scope of these umpolung α-arylation reactions has yet to be fully realized.

Over the past five years, our group has explored the reactivity of oxyallyl cation intermediates generated in the formal homo-Nazarov cyclization (ring-opening cyclization of alkenyl cyclopropyl ketones) to access functionalized cyclohexanones, cyclohexenols, and phenols.[9] In addition, we recently disclosed the first example of a catalytic, interrupted formal homo-Nazarov cyclization in the presence of allylsilanes.[9a] In that report, the oxyallyl cation intermediate reacts with allyl TMS using catalytic $SnCl_4$ to form α-allylcyclohexanones. Additionally, hexahydrobenzofurans were preferentially obtained with stoichiometric $SnCl_4$ and allyl TBDPS via a formal [3+2] cycloaddition pathway. Given this success, we have now sought to expand the interrupted formal homo-Nazarov cyclization to include other nucleophilic trapping agents, with particular interest on arenes and heteroarenes.

Scheme 1. Arylative Interrupted Nazarov vs. Formal Homo-Nazarov Cyclization



Toward this endeavor, we were inspired by seminal work from West[10] and others[11] on the interrupted Nazarov cyclization. In these contributions, various examples of inter- and intramolecular aryl trapping of the cyclopentyl oxyallyl cation were disclosed (Scheme 1A). We

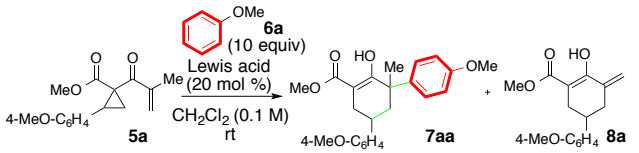
envisioned a homologous strategy to access functionalized α-(hetero)aryl cyclohexanones involving the Friedel-Crafts-type reactions of various arenes and heteroarenes with the six-membered, cyclic oxyallyl cations **I** generated through formal homo-Nazarov cyclizations (Scheme 1B). Lewis acid-activation of donor-acceptor-acceptor (D-A-A) cyclopropanes results in a ring-opening cyclization to form an initial acyclic zwitterionic intermediate. Subsequent intramolecular π-attack generates oxyallyl cations **I** which react with (hetero)arenes to provide α-(hetero)aryl cyclohexanones. Most importantly, regiospecific arylation at C-3 of intermediate **I** is expected due to the electron-withdrawing ester's influence on the polarization of the oxyallyl cation.[12]

RESULTS AND DISCUSSION

Our reaction optimization began with cyclopropyl vinyl ketone **5a** as the model substrate with anisole (**6a**) as the aromatic nucleophile (Table 1). Fortuitously, our previously reported allylsilane-trapping conditions (20 mol % $SnCl_4$, 10 equivalents of nucleophile, CH_2Cl_2, 25 ˚C), proved ideal and the desired α-arylated homo-Nazarov product **7aa** was obtained in 67% yield as a complex keto-enol mixture of diastereomers. Consistent with reported and theoretical Friedel-Crafts reactions of anisoles, only the 4-alkylated regioisomer was observed.[13] Other catalysts gave either decreased selectivity toward the arylated product or extended reaction times (entries 2-6). For instance, $In(OTf)_3$ favored the eliminative (untrapped) homo-Nazarov product **8a** and gave only 11% yield of **7aa** (entry 2), whereas $InCl_3$ gave 69% yield but with reduced selectivity and a longer reaction time (entry 3). Improved outcomes were not observed upon decreasing the catalyst loading and/or the equivalents of anisole. Similarly, no improvement was seen by

altering the reaction solvent or concentration (see Supporting Information). Attempts to shift the keto-enol equilibrium toward either the keto or enol tautomer also failed to achieve any tenable results.

Table 1. Reaction Optimization



entry	Lewis acid	time (h)	**7aa**/**8a**[b]	yield of **7aa** (%)[c]
1	**$SnCl_4$**	**1**	**22.3:1**	**67**
2	$In(OTf)_3$	1	1:1.7	11
3	$InCl_3$	24	11.5:1	69
4	$Sc(OTf)_3$	1	2.3:1	10
5	$Al(OTf)_3$	72	0:1	--[d]
6	$Mg(OTf)_2$	27	5.7:1	63

[a] Reactions were performed with 20 mol % Lewis acid, 10 equiv of anisole, and 1 equiv of cyclopropane **5a** in CH_2Cl_2 (0.1 M) at 25 ˚C. [b] Ratios determined by ^{1}H NMR. [c] Isolated yield of keto/enol isomer mixture after column chromatography. [d] Not determined.

Given the complex keto-enol mixture, we were unable to unequivocally determine the absolute diastereoselectivity directly for **7aa**. An estimate of the diastereoselectivity could be inferred from the ratios of enol H's using ^{1}H NMR (11:1 *dr*, Figure 1A). However, an easily exchangeable proton is usually not an ideal marker for determining ratios. This concern was confirmed by subjecting **7aa** to Krapcho decarbalkoxylation conditions and measuring the diastereomeric ratio for product **9aa** using ^{1}H NMR of the crude reaction mixture (Figure 1B). **9aa** was obtained as a 7.7:1 diastereomeric mixture, which was later confirmed upon isolation. Thus, although an initial estimate of diastereoselectivity could be made directly for **7aa**, it did not reflect the actual ratio (11:1 vs 7.7:1). Toward that end, for the remainder of the study, all

diastereoselectivities were quantified and extrapolated to the keto-enol mixtures using the crude Krapcho products. Nevertheless, in the cases where **7aa** will be carried forward for further derivatization, the enol proton can still be used as a qualitative estimate.[14]

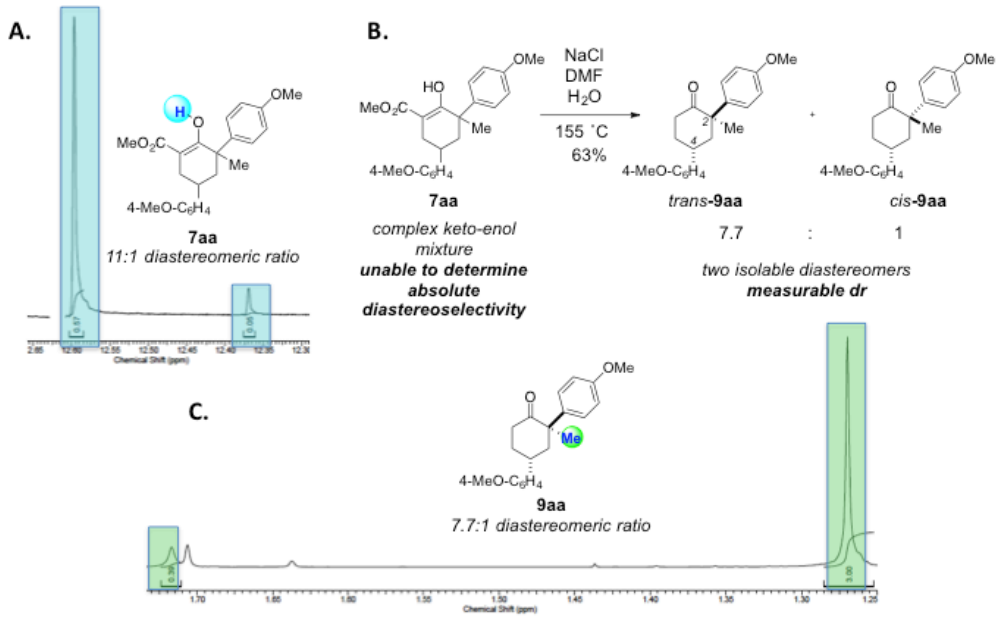
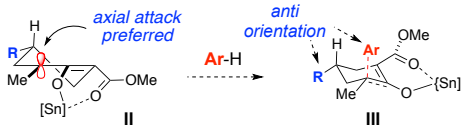


Figure 1. Determining Diastereoselectivity using ^{1}H NMR

For **9aa**, the major diastereomer had the two aryl substituents at C-2 and C-4 *anti* relative to one another (Scheme 2).[15] This outcome can be rationalized using a modified cyclohexa-1,3-diene twist-chair conformation according to the Fürst-Plattner Rule.[16] During the formation of **7aa**, aryl attack on the Sn-oxyallyl cation complex **II** is expected to occur in an axial fashion in order to achieve the preferred chair-like transition state (**III**). The *anti* orientation between the two aryl groups minimizes destabilizing 1,3-axial-pseudoaxial interactions upon aryl attack.[17] This destabilization is more pronounced in the formation of the minor diastereomer. This

diastereoselectivity is consistent with our previous observations in the allylative, interrupted formal homo-Nazarov cyclization.[9a]

Scheme 2. Rationale for Stereochemical Outcome

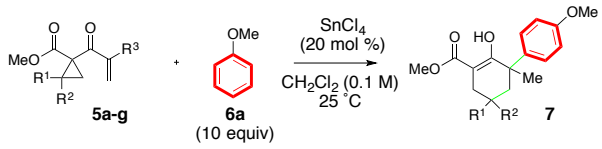


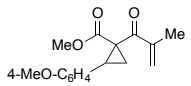
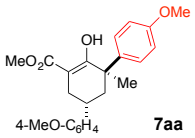
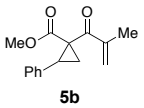
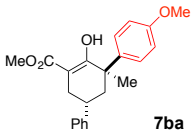
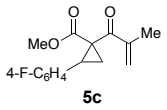
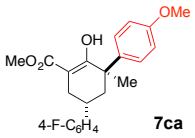
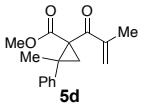
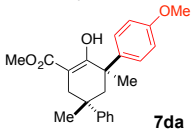
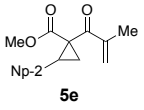
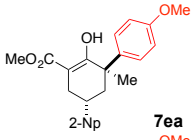
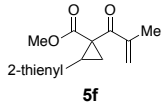
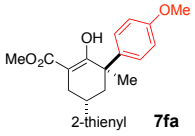
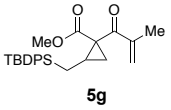
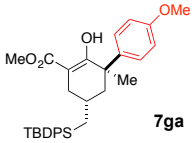
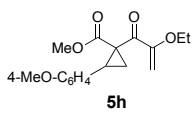
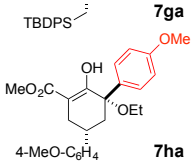
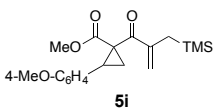
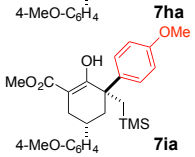
Next, the reactivity of anisole with various cyclopropanes under the optimized conditions was examined (Table 2). Compared to **5a**, phenyl cyclopropane **5b** gave a reduced yield (44%) of the expected arylated product **7ba** with a 11.7:1 *dr*. 4-Fluorophenylcyclopropane **5c** afforded the desired product **7ca** in 56% yield with a 10.5:1 *dr*. These product outcomes are consistent with expected Hammett parameters for benzylic carbocation stability.[18] The *gem*-disubstituted methylphenyl cyclopropane **5d** provided **7da** in 44% yield with a 2.0:1 *dr*. This modest yield was unanticipated as we expected **5d** to perform better than **5b** due to the added stabilization from the *gem*-methyl group onto the benzylic carbocation intermediate. However, significant product degradation was also observed. Good product yield (77%) and diastereoselectivity (8.3:1 *dr*) for **7ea** was observed with the 2-naphthylcyclopropane **5e**. Aryl-trapped product **7fa** was formed in 56% yield with a 5.5:1 *dr* from (2-thienyl)cyclopropane **5f**.

Employing a non-aromatic cation-stabilizing donor on the cyclopropane (as in the silylmethyl group in **5g**) gave 57% yield of **7ga** with good diastereoselectivity (11.2:1 dr). Cyclopropanes **5h** and **5i**, respectively bearing an α-ethoxy or α-methylenesilyl substituent on the alkene, both gave the undesired eliminative homo-Nazarov products and/or copious amounts of indiscernible degradation products. The extra carbocation stabilization provided by the heteroatom in **5h** presumably reduces the electrophilicity of the oxyallyl cation thus hindering

nucleophilic trapping, whereas the lability of the silyl group in **5i** results in rapid formation of the eliminative product.[12,19]

Table 2. Catalytic, interrupted, formal homo-Nazarov cyclizations with anisole.

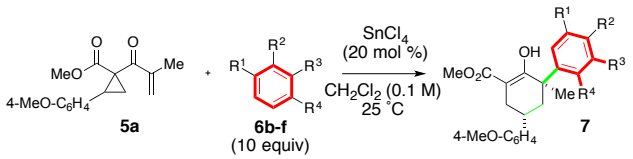


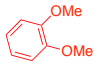
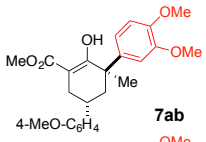
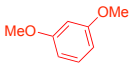
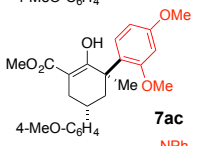
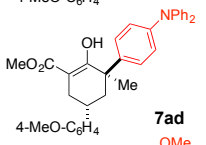
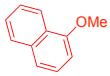
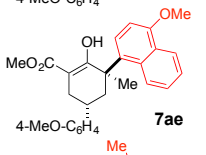
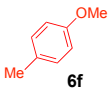
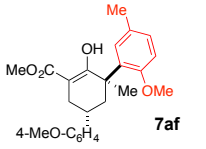
entry[a]	Cyclopropane	Product	yield (%)[b]	dr[c]
1	 **5a**	 **7aa**	72 (63)	7.7:1
2	 **5b**	 **7ba**	44 (58)	12:1
3	 **5c**	 **7ca**	56 (57)	11:1
4	 **5d**	 **7da**	44 (61)	2.0:1
5	 **5e**	 **7ea**	77 (77)	8.3:1
6	 **5f**	 **7fa**	56 (76)	5.5:1
7	 **5g**	 **7ga**	57 (68)	11:1
8	 **5h**	 **7ha**	--[d]	--[e]
9	 **5i**	 **7ia**	--[d]	--[e]

[a] Reactions were performed with cyclopropane **5** (1 equiv), arene **6** (10 equiv), and $SnCl_4$ (20 mol %) in CH_2Cl_2 (0.1 M) at 25 ˚C. [b] Isolated yield after column chromatography. Numbers in parentheses represent yields of Krapcho decarbalkoxylation products **9**. [c] Diastereomeric ratios determined by ^1H NMR on the decarbalkoxylated products. [d] No desired product formed [e] Not determined.

Other arenes were then employed to further probe the generality of the transformation (Table 3). 1,2-Dimethoxybenzene (**6b**) is alkylated at its 4-position to give the expected product **7ab** in 72% yield with a 5.3:1 *dr* (entry 1). With 1,3-dimethoxybenzene (**6c**), two regioisomeric products are possible; although only one product **7ac** (alkylation at more sterically-accessible C-4) was obtained in 62% yield and a 6.8:1 *dr* (entry 2). Triphenylamine (**6d**) proved to be a competent nucleophile providing **7ad** in 71% yield and a 2.0:1 *dr* (entry 3). The 4-alkylated product **7ae** was isolated in 70% yield with a *dr* of 1.2:1 from the reaction with 1-methoxynaphthalene (**6e**, entry 4). 4-Methylanisole (**6f**) gave a low yield (15%) of **7af** (entry 5). In this case, as compared to **7ac**, steric hindrance presumably overrides any electronic preference for reactivity. Less electron-rich arenes, such as benzene, toluene, halobenzenes, 3-bromoanisole, and TMS benzene, failed to provide tractable amounts of α-arylated products (Figure 2). In these cases, varying amounts of the eliminative homo-Nazarov product and a putative chloride-trapping product were observed.

Table 3. Reactions with various arenes.



entry[a]	Arene	Product	yield (%)[b]	dr[c]
1	 **6b**	 **7ab**	72 (85)	5.3:1
2	 **6c**	 **7ac**	88 (89)	6.8:1
3	 **6d**	 **7ad**	71 (58)	2.0:1
4	 **6e**	 **7ae**	70 (78)	1.2:1
5	 **6f**	 **7af**	15 (--)[d]	--[e]

[a] Reactions were performed with cyclopropane **5** (1 equiv), arene **6** (10 equiv), and $SnCl_4$ (20 mol %) in CH_2Cl_2 (0.1 M) at 25 °C. [b] Isolated yield after column chromatography. Numbers in parentheses represent yields of Krapcho decarbalkoxylation products **9**. [c] Diastereomeric ratios determined by ^1H NMR on the decarbalkoxylated products. [d] No desired Krapcho product isolated. [e] Not determined.

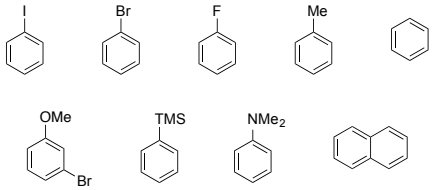
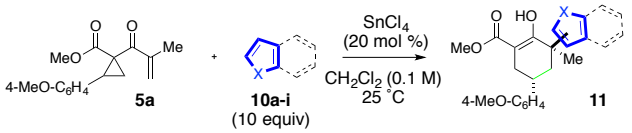


Figure 2. Unsuccessful arene trapping agents

Given the success with arenes, we moved on to employing heteroarenes as the nucleophiles under the same reaction conditions (Table 4). Furan (**10a**) and thiophene (**10b**) both gave their expected 2-alkylated products **11aa** and **11ab** in 66% and 74% yield with *dr*'s of 1.8:1 and 4:3:1, respectively (entries 1 and 2). The observed regioselectivity is consistent with both the Friedel-Crafts reactivity of furan/thiophene[20] and the observations by West[10a] for the interrupted Nazarov cyclization. 2-Methoxythiophene (**10c**) afforded the 5-alkylated regioisomer **11ac** in 75% yield and a 1.3:1 *dr* (entry 3). 2,5-Dimethylfuran (**10d**) and –thiophene (**10e**) provided their respective products **11ad** and **11ae** in 46% and 87% yield (entries 4 and 5). Due to the instability of 2,5-dimethylfuran in the presence of $SnCl_4$, the reaction was performed with $InCl_3$ (10 mol %). Benzothiophene (**10f**) was readily alkylated at the more nucleophilic C-3 position to form **11af** in 73% yield and a 2.3:1 *dr* (entry 6). Similarly, *N*-tosyl indole (**10h**) afforded **11ah** in 69% yield and a 2.6:1 *dr* (entry 7). Blocking C-3 on *N*-tosyl indole with a methyl group (as in **10i**) gave only trace amount of product **11ai** (entry 8). This outcome is most likely due to the combination of the reduced nucleophilicity at C-2 and the steric influence of the methyl group. Finally, no alkylated product was observed with *N*-tosyl- or *N*-methylpyrrole (entries 9 and 10).

Table 4. Reactions using heteroarenes as nucleophiles

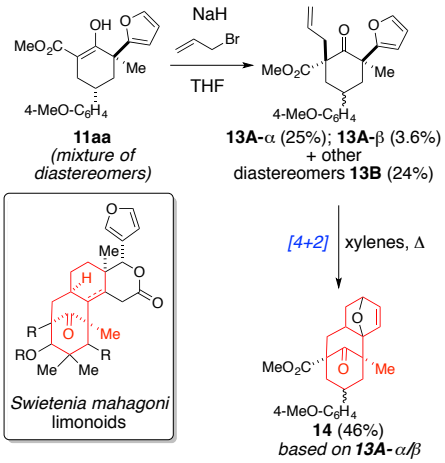


entry[a]	Heteroarene	Product	yield (%)[b]	dr[c]
1	**10a** (X = O)	**11aa** (X = O)	66 (32)	1.8:1
2	**10b** (X = S)	**11ab** (X = S)	74 (52)	4.3:1
3	**10c**	**11ac**	75 (70)	1.3:1
4	**10d** (X = O)	**11ad** (X = O)	48[d] (42)	3.8:1
5	**10e** (X = S)	**11ae** (X = S)	87 (71)	4.1:1
6	**10f** (X = S)	**11af** (X = S)	73 (62)	2.3:1
7	**10g** (X = NTs)	**11ag** (X = NTs)	69 (78)	2.6:1
8	**10h**	**11ah**	trace	--[e]
9	**10i** (R = Ts)	**11ai** (R = Ts)	--[f]	--[e]
10	**10j** (R = Me)	**11aj** (R = Me)	--[f]	--[e]

[a] Reactions were performed with cyclopropane **5** (1 equiv), arene **10** (10 equiv), and $SnCl_4$ (20 mol %) in CH_2Cl_2 (0.1 M) at 25 °C. [b] Isolated yield after column chromatography. Numbers in parentheses represent yields of Krapcho decarbalkoxylated products **12**. [c] Diastereomeric ratios determined by ^1H NMR on the decarbalkoxylated products. [d] Performed using 10 mol % $InCl_3$ instead of $SnCl_4$. [e] Not determined. [f] No desired product formed.

To showcase the utility of the α-(hetero)arylated products as synthetic building blocks, we were inspired by the work of Padwa on intramolecular Diels-Alder reactions of alkylated furans tethered to alkenes.[21] Toward that end, we sought to initiate a subsequent intramolecular [4+2] cycloaddition with furan product **11aa** following α'-allylation. This sequence, if successful, would form a functionalized tricycle that should allow access into the tetracyclic core of the *Swietenia mahagoni* liminoids.[22] When treated with NaH and allyl bromide, **11aa** underwent allylation in 53% yield to give **13** as a 7.1:3.6:3.1:1.0 mixture of diastereomers (Scheme 3).[23] In agreement with our previous work,[9a] the major diastereomer from the allylation has the allyl and furan groups *syn* to one another (i.e., **13A-α**). **13A-α** and the other *syn* diastereomer, **13A-β**, are both expected to undergo intramolecular cycloaddition, whereas the diastereomers with the allyl and furan groups *anti* to one another (**13B-α** and **13B-β**) will not react. When the mixture was heated in xylenes at reflux, the desired [4+2] cycloadduct **14** was obtained in 46% yield (based on **13A-α/β**) as a 5.3:1 mixture of diastereomers. Full conversion was not achieved as some unreacted **13A-α/β** was recovered along with what appears to be some starting material/product degradation.[24]

Scheme 3. α'-Allylation and attempted intramolecular Diels-Alder cycloaddition of **11aa**



In summary, we have developed a catalytic protocol for the interrupted, formal homo-Nazarov cyclization using a range of electron-rich arenes and heteroarenes as nucleophiles for trapping the six-membered oxyallyl cationic intermediate. The methodology provides facile access to densely functionalized α-(hetero)aryl cyclohexanones in a single step from donor-acceptor-acceptor cyclopropanes. α-(Hetero)arylated products are formed regiospecifically, and in up to 88% yield and diastereoselectivities up to 12:1. A number of different cyclopropanes are viable for reactivity. This cascade transformation represents the first example of a (hetero)arylative, interrupted homo-Nazarov cyclization. Further work on the intramolecular, (hetero)arylative capture of oxyallyl cations in the homo-Nazarov reaction is currently underway. Application of the method toward specific bioactive natural product targets will be reported in due course.

EXPERIMENTAL SECTION

General Information. Chromatographic purification was performed as flash chromatography with silica gel (40-65μm) or preparative thin-layer chromatography (prep-TLC) using silica gel F_{254} (1000 μm) plates and solvents indicated as eluent with 0.1-0.5 bar pressure. For quantitative

flash chromatography, technical grades solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 μm F_{254} TLC glass plates. Visualization was accomplished with UV light. Infrared (IR) spectra were obtained using FTIR with an ATR attachment by attenuated total reflection through a diamond plate. The IR bands are characterized as weak (w), medium (m), and strong (s). Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on 300 MHz, 400 MHz, and 500 MHz spectrometers with solvent resonances as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). ^{19}F NMR spectra were recorded on 400 and 500 MHz spectrometers using $PhCF_3$ as an external standard. ^{1}H, ^{13}C, and ^{19}F NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, t = triplet, tt = triplet of triplets, m = multiplet, br = broad), coupling constants (Hz), and integration. The accurate mass analyses were run in EI mode on a double focusing magnetic sector mass spectrometer at a mass resolution of 10,000 using PFK (perfluorokerosene) as an internal calibrant or in ESI mode using a hybrid linear ion trap/orbitrap tandem mass spectrometer. Uncorrected melting points were measured with a digital melting point apparatus.

Reaction Optimizations Procedures.

Procedure for Catalyst Screening. To a dry flask charged with a stir bar and DCM was added the Lewis acid (20 mol %) under nitrogen. Anisole (10.0 equiv) was added. Finally, cyclopropane **5a** (1.0 equiv, as a solution in DCM) was added, drop-wise, to mixture at the room temperature. The volume of solvent used was such that the final concentration of cyclopropane in DCM was 0.1 M.

The reaction was monitored by TLC until complete conversion of cyclopropane was observed. Upon reaching completion, the reaction was then quenched with distilled water (3 mL), and extracted with DCM three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel flash chromatography using EtOAc/Hexane as the eluent.

Procedure for Optimization of Catalyst Loading. To a dry flask charged with a stir bar and DCM was added the applicable loading of $SnCl_4$ or $InCl_3$ under nitrogen. Anisole (10.0 equiv) was added. Finally, cyclopropane **5a** (1.0 equiv, as a solution in DCM) was added, drop-wise, to mixture at the room temperature. The volume of solvent used was such that the final concentration of cyclopropane in DCM was 0.1 M. The reaction was monitored by TLC until complete conversion of cyclopropane was observed. Upon reaction completion, the reaction was then quenched with distilled water (3 mL), and extracted with DCM three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel flash chromatography using EtOAc/Hexanes as the eluent.

Procedure for Anisole Loading Screening. To a dry flask charged with a stir bar and DCM was added the appropriate loading of anisole and $SnCl_4$ (20 mol %). Finally, cyclopropane **5a** (1.0 equiv, as a solution in DCM) was added, dropwise, to the mixture at the room temperature. The volume of solvent used was such that the final concentration of cyclopropane in DCM was 0.1 M. The reaction was monitored by TLC until complete conversion of cyclopropane was observed. Upon reaction completion, the reaction was then quenched with distilled water (3 mL), and extracted with DCM three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel flash chromatography using EtOAc/Hexanes as the eluent.

Procedure for Temperature and Solvent Screening. To a dry flask charged with a stir bar and the applicable solvent was added 20 mol% $SnCl_4$ under nitrogen. Anisole (10.0 equiv) was added.

Finally, cyclopropane **5a** (1.0 equiv, as a solution in appropriate solvent) was added, drop-wise, to the mixture at room temperature. In the temperature screening, DCM was used as the solvent. The volume of solvent used was such that the final concentration of cyclopropane in the appropriate solvent was 0.1 M. The reaction was monitored by TLC until complete conversion of cyclopropane was observed. Upon reaching completion, the reaction was quenched with distilled water (3 mL), and extracted with DCM three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel flash chromatography using EtOAc/Hexanes as the eluent.

Synthesis of Trapping Agents. 1-Methoxynaphthalene (**6e**) was prepared according to a previously reported procedure.[25]

***N*-Tosyl indole (10g):** Adapted from a reported procedure.[26a] Indole (500 mg, 4.26 mmol) as a solution in THF (10 mL) was added to a suspension of NaH (256 mg as a 60% suspension in mineral oil, 6.40 mmol) in THF (10 mL) and stirred for 30 min. Tosyl chloride (900 mg, 4.72 mmol) was added as a solution in THF (5 mL) and stirred overnight. Water was slowly added, EtOAc added, and the organic layer was washed with sat. aq. $NaHCO_3$, brine, and dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel to give N-tosylindole (1.14 g, 98% yield). Characterization was consistent with that reported.[27]

***N*-Tosyl-3-methylindole (10h):** Adapted from a reported procedure.[26a] 3-methylindole (1.00 g, 7.62 mmol) as a solution in THF (20 mL) was added to a suspension of NaH (666 mg as a 60% suspension in mineral oil, 16.65 mmol) in THF (20 mL) and stirred for 30 min. Tosyl chloride (1.60 g, 8.38 mmol) was added as a solution in THF (10 mL) and stirred overnight. Water was slowly added, EtOAc added, and the organic layer was washed with sat. aq. $NaHCO_3$, brine, and

dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel to give *N*-tosyl-3-methylindole (1.94 g, 89% yield). Characterization was consistent with that reported.[26b]

***N*-Tosyl pyrrole (10i):** Prepared using a modification of a patented procedure.[28] Pyrrole (1.00 g, 15 mmol) as a solution in THF (4 mL) was added to a suspension of NaH (900 mg as a 60% suspension in mineral oil, 22.5 mmol) in THF (4 mL) and stirred for 30 min. Tosyl chloride (2.84 g, 15 mmol) was added as a solution in THF (4 mL) and stirred for 3 h. Water was slowly added, and the organic layer was separated, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel. Characterization was consistent with that reported.[28]

Synthesis of Cyclopropyl Malonates.

Dimethyl 2-((*tert*-butyldiphenylsilyl)methyl)cyclopropane-1,1-dicarboxylate (15g): Prepared according to our previously reported conditions.[9a] Rh_2esp_2 (2 mg, 3 μmol) was dissolved in DCM (2.05 mL) and allyl-TBDPS was added (1.18 mL, 4.11 mmol). After cooling to 0 ˚C, diazodimethylmalonate (500 mg, 3.15 mmol) was added as a solution in DCM (2.05 mL). The solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched with sat. aq. thiourea, extracted three times with DCM, and the organic layer was washed with brine. The organic mixture was then dried over Na_2SO_4, filtered, and concentrated. The crude mixture was then purified by column chromatography on silica gel (10% EtOAc/Hexane, R_f = 0.36) to give the cyclopropane **15g** as a colorless oil (1.19 g, 92% yield). All characterization was consistent with those previously published.[29]

Dimethyl 2-(thiophen-2-ylmethylene)malonate (16): Prepared using our previously reported procedure.[30] Dimethylmalonate (1.00 g, 7.57 mmol) was dissolved in benzene (15 mL). Thiophene-2-carboxaldehyde (0.90 mL, 9.84 mmol), piperidine (0.15 mL, 1.51 mmol), and acetic acid (0.22 mL, 3.78 mmol) were added. The reaction was heated to reflux with a Dean-Stark apparatus for 4 h. The reaction was then concentrated. After water was added, the reaction was extracted three times with EtOAc, washed with 1M HCl, sat. aq. $NaHCO_3$, and brine sequentially, dried over Na_2SO_4, filtered, and concentrated. The mixture was purified by column chromatography on silica gel (20% EtOAc/Hexanes, R_f = 0.44) to give the unsaturated diester **16** as a yellow oil (1.77g, >99% yield). **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.89 (d, J = 0.6 Hz, 1 H), 7.55 - 7.52 (m, 1 H), 7.38 - 7.36 (m, 1 H), 7.10 - 7.07 (m, 1 H), 3.93 (s, 3 H), 3.83 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 166.6, 164.7, 135.9, 135.5, 134.7, 131.9, 127.8, 121.5, 52.8, 52.6. **IR:** 2951 (w), 1719 (s), 1612 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{10}H_{10}O_4S$ 226.0300; Found 226.0302.

Dimethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (15f): Prepared using a previously reported procedure.[31] Sodium hydride (195 mg as 60% suspension in mineral oil, 4.86 mmol) was dissolved in DMSO (8.8 mL), and trimethylsulfoxonium iodide (1.07 g, 4.86 mmol) was added in one portion at room temperature and stirred for 30 min. Compound **16** (1.00 g, 4.42 mmol) was added in one portion as a solution in DMSO (1.8 mL) at room temperature and stirred for 30 min. The reaction was quenched with water at 0 ˚C, extracted five times with diethyl ether, washed five times with water, dried over sodium sulfate, and concentrated. The resulting mixture was purified by column chromatography on silica gel (20% EtOAc/Hexanes, R_f = 0.52) to give the cyclopropane **15f** as a yellow oil (591 mg, 56% yield). **^{1}H NMR** (300MHz, $CDCl_3$) δ = 7.18 - 7.14 (m, 1 H), 6.90 (dd, J = 3.5, 5.1 Hz, 1 H), 6.85 - 6.82 (m, 1 H), 3.78 (s, 3

H), 3.48 (s, 3 H), 3.32 - 3.25 (m, 1 H), 2.17 - 2.12 (m, 1 H), 1.86 - 1.80 (m, 1 H). **^{13}C NMR** (75MHz, $CDCl_3$) δ = 169.7, 166.7, 138.0, 126.7, 126.2, 125.1, 52.9, 52.5, 37.8, 27.3, 21.0. **IR:** 2951 (w), 1721 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{11}H_{12}O_4S$ 240.0456; Found 240.0468.

Synthesis of Cyclopropyl Vinyl Ketones. Cyclopropyl vinyl ketones **5a-e**, **5h**, and **5i** were prepared according to our previously reported conditions. All characterizations were in agreement with those previously published. [9a,9c]

Methyl 1-methacryloyl-2-(thiophen-2-yl)cyclopropane-1-carboxylate (5f): Prepared according to our previously reported conditions.[9a,9c] Compound **15f** (580 mg, 2.41 mmol) dissolved in THF (6.2 mL) and isopropenylmagnesium bromide (5.8 mL as 0.5 M solution in THF, 2.90 mmol) were stirred for 2 h at -78°C. The reaction was quenched with sat. aq. NH_4Cl, extracted three times with EtOAc, acidified to pH=4 with HCl, and extracted a final time with EtOAc. After drying with Na_2SO_4, filtering, and concentrating, the reaction was purified by flash chromatography on silica gel (10% EtOAc/Hexanes, R_f = 0.44) and **5f** was given as a colorless oil (398 mg, 65% yield). (*Diastereomeric ratio* = 2.7:1) **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.15 (dd, *J* = 1.1, 5.0 Hz, 0.37 H), 7.07 (dd, *J* = 1.1, 5.0 Hz, 1 H), 6.91 (dd, *J* = 3.7, 5.2 Hz, 0.41 H), 6.89 - 6.87 (m, 0.41 H), 6.84 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.65 (td, *J* = 0.9, 3.7 Hz, 1 H), 5.91 (d, *J* = 0.9 Hz, 0.37 H), 5.74 - 5.71 (m, 1.47 H), 5.64 - 5.62 (m, 1 H), 3.71 (s, 3 H), 3.50 - 3.45 (m, 2.28 H), 3.44 - 3.39 (m, 0.41 H), 2.27 (dd, *J* = 4.7, 7.8 Hz, 0.41 H), 2.18 (dd, *J* = 5.0, 7.8 Hz, 1 H), 1.96 - 1.94 (m, 1.12 H), 1.76 (dd, *J* = 5.0, 9.3 Hz, 1 H), 1.74 (dd, *J* = 0.9, 1.5 Hz, 3 H), 1.61 (dd, *J* = 4.9, 9.2 Hz, 0.47 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 195.7, 193.6, 171.2, 168.6, 144.3, 144.1, 138.3, 138.0, 126.8, 126.6, 126.6, 125.5, 125.2, 124.8, 124.4, 124.0, 52.6, 52.4, 42.3, 41.6,

28.4, 24.9, 21.7, 20.4, 17.9, 17.4. **IR:** 2953 (w), 1724 (s), 1670 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{13}H_{14}O_3S$ 250.0664; Found 250.0666.

(1*R*,2*S*)/(*1S*,*2R*)-Methyl 2-((*tert*-butyldiphenylsilyl)methyl)-1-methacryloylcyclopropane-1-carboxylate (5g): Prepared according to our previously reported conditions.[9a,9c] Cyclopropane **15g** (979 mg, 2.38 mmol) dissolved in THF (6.3 mL) and isopropenylmagnesium bromide (5.8 mL from 0.5 M solution in THF, 2.90 mmol) were stirred for 1 h at -78 ˚C. The reaction was quenched with sat. aq. NH_4Cl, extracted three times with EtOAc, acidified to pH=4 with HCl, and extracted a final time with EtOAc. After drying with Na_2SO_4, filtering, and concentrating, the reaction was purified by flash chromatography on silica gel (10% EtOAc/Hexanes, R_f = 0.47) and **5g** was given as a colorless oil (500 mg, 50% yield). **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.64 - 7.60 (m, 4 H), 7.42 - 7.32 (m, 6 H), 5.74 (s, 1 H), 5.60 - 5.59 (m, 1 H), 3.68 (s, 3 H), 2.04 - 1.96 (m, 1 H), 1.85 (t, J = 1.1 Hz, 3 H), 1.50 (dd, J = 3.2, 14.8 Hz, 1 H), 1.28 - 1.24 (m, 1 H), 1.18 (dd, J = 11.3, 15.0 Hz, 1 H), 1.06 (s, 9 H), 1.00 (dd, J = 4.6, 9.2 Hz, 1 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 197.1, 170.7, 144.5, 136.1, 136.0, 134.3, 134.0, 129.2, 129.2, 127.7, 127.6, 127.5, 123.1, 77.3, 76.7, 52.2, 39.6, 27.8, 27.8, 24.1, 24.0, 18.1, 17.9, 8.4. **IR:** 2953 (w), 2929 (w), 2887 (w), 2856 (w), 1728 (s), 1672 (s) cm^{-1}. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{26}H_{33}O_3Si$ 421.2193; Found 421.2185.

(1*R*,2*R*)/(1*S*,2*S*)-Methyl 2-((*tert*-butyldiphenylsilyl)methyl)-1-methacryloylcyclopropane-1-carboxylate (*epi*-5g): Prepared according to our previously reported conditions.[9a,9c] Cyclopropane **15g** (979 mg, 2.38 mmol) dissolved in THF (6.3 mL) and isopropenylmagnesium bromide (5.8 mL from 0.5 M solution in THF, 2.90 mmol) were stirred for 1 h at -78 ˚C. The reaction was quenched with sat. aq. NH_4Cl, extracted three times with EtOAc, acidified to pH=4 with HCl, and extracted a final time with EtOAc. After drying with Na_2SO_4, filtering, and

concentrating, the reaction was purified by flash chromatography on silica gel (10% EtOAc/Hexanes, R_f = 0.39) and ***epi*-5g** was given as a colorless oil (251 mg, 25% yield). **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.60 - 7.56 (m, 4 H), 7.42 - 7.33 (m, 6 H), 5.80 - 5.78 (m, 1 H), 5.78 - 5.76 (m, 1 H), 3.59 (s, 3 H), 2.13 - 2.06 (m, 1 H), 1.97 (dd, *J* = 0.9, 1.5 Hz, 3 H), 1.49 (dd, *J* = 2.4, 14.6 Hz, 1 H), 1.19 (dd, *J* = 4.6, 7.6 Hz, 1 H), 1.04 - 1.01 (m, 10 H), 0.48 (dd, *J* = 12.2, 14.6 Hz, 1 H). ^{13}C NMR (126MHz, $CDCl_3$) δ = 196.3, 172.3, 145.7, 136.0, 135.9, 134.0, 133.9, 129.3, 127.7, 127.6, 124.3, 52.2, 38.6, 27.8, 26.2, 22.6, 18.1, 17.8, 9.8. **IR:** 2957 (w), 2928 (w), 2857 (w), 1726 (s), 1674 (s) cm^{-1}. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{26}H_{33}O_3Si$ 421.2193; Found 421.2185.

Synthesis of (Hetero)arylated Homo-Nazarov Products.

General Procedure: To a dry flask charged with a stir bar, 4 Å molecular sieves, and CH_2Cl_2 was added the appropriate arene or heteroarene (10 equiv.) and cyclopropane (1.0 equiv., as a solution in CH_2Cl_2). The final volume of CH_2Cl_2 used was such that the concentration of cyclopropane in CH_2Cl_2 was 0.1 M. $SnCl_4$ (20 mol %) was added dropwise or $InCl_3$ (10 mol %) all at once and the reaction was stirred at room temperature (unless otherwise noted) until the cyclopropane was consumed (as monitored by TLC). The reaction was quenched with water (3 mL) and extracted three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude mixture was purified by silica gel flash chromatography unless noted as being purified by preparatory thin-layer chromatography using EtOAc/hexanes as the eluent.

Methyl 6'-hydroxy-4,4''-dimethoxy-1'-methyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7aa): Prepared following general procedure using cyclopropane **5a** (100 mg,

0.37 mmol), anisole (0.40 mL, 3.65 mmol), and $SnCl_4$ (9 µL, 0.07 mmol) in CH_2Cl_2 (3.7 mL) stirred at room temperature for 1 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.29), cyclohexenol **7aa** was given as a colorless oil (94 mg, 67% yield). *Complex mixture of keto-enol tautomers and diastereomers.* **^{1}H NMR** (300MHz, $CDCl_3$) δ = 12.60 (s, 0.57 H), 7.30 - 7.23 (m, 2.23 H), 7.22 - 7.14 (m, 4.52 H), 7.07 - 7.01 (m, 1.65 H), 7.00 - 6.95 (m, 2.15 H), 6.91 - 6.83 (m, 4.16 H), 6.83 - 6.77 (m, 1.72 H), 3.84 (s, 2.91 H), 3.81 - 3.79 (m, 8.20 H), 3.77 (d, *J* = 2.8 Hz, 6.27 H), 3.27 - 3.15 (m, 1.26 H), 2.77 (dt, *J* = 3.3, 14.4 Hz, 1.11 H), 2.68 (dd, *J* = 1.7, 5.2 Hz, 0.35 H), 2.65 - 2.52 (m, 1.36 H), 2.37 - 2.15 (m, 3.02 H), 2.15 - 1.96 (m, 3.16 H), 1.61 (s, 2.32 H), 1.29 (s, 3.00 H). **^{13}C NMR** (75MHz, $CDCl_3$) δ = 208.4, 174.9, 173.3, 170.5, 158.5, 158.4, 157.9, 157.8, 138.2, 137.6, 135.7, 134.3, 127.6, 127.6, 127.5, 127.0, 114.8, 114.0, 113.7, 113.5, 98.7, 55.3, 55.2, 55.2, 54.1, 54.0, 52.0, 51.6, 46.4, 45.8, 45.0, 37.8, 37.1, 34.4, 32.0, 28.4, 27.1. **IR:** 2931 (w), 1746 (m), 1714 (m), 1653 (m), 1611 (m), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{23}H_{26}O_5$ 382.1780; Found 382.1765.

Methyl 6'-hydroxy-4-methoxy-1'-methyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7ba): Prepared following the general procedure using cyclopropane **5b** (104 mg, 0.42 mmol), anisole (0.44 mL, 4.09 mmol), and $SnCl_4$ (9 µL, 0.07 mmol) in CH_2Cl_2 (4.2 mL) stirred at room temperature for 1 h. After work-up and purification by prepTLC (10% EtOAc/Hexanes, R_f = 0.48), cyclohexenol **7ba** was given as a colorless oil (66 mg, 44% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.59 (s, 0.90 H), 12.36 (s, 0.14 H), 7.35 - 7.30 (m, 1.87 H), 7.28 - 7.21 (m, 7.89 H), 7.18 - 7.13 (m, 2.85 H), 7.12 - 7.08 (m, 1.95 H), 6.98 - 6.94 (m, 1.67 H), 6.88 - 6.82 (m, 2.30 H), 3.82 (s, 2.62 H), 3.79 - 3.77 (m, 6.49 H), 3.77 - 3.75 (m, 3.46 H), 3.74 (s, 0.23 H), 3.70 (s, 0.14 H), 3.23 (tt, *J* = 3.3, 12.7 Hz, 0.93 H), 3.12 - 2.99 (m, 0.24 H), 2.78 (dt, *J* = 3.2, 14.6 Hz, 1.01 H), 2.70 -

2.59 (m, 2.04 H), 2.39 - 2.29 (m, 1.84 H), 2.26 - 2.18 (m, 1.02 H), 2.17 - 2.10 (m, 1.18 H), 2.09 - 1.99 (m, 2.21 H), 1.76 (s, 0.51 H), 1.59 (s, 3.00 H), 1.28 (s, 2.66 H), 1.25 - 1.19 (m, 0.84 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 208.3, 174.9, 173.3, 170.5, 158.5, 157.9, 145.5, 143.6, 138.1, 134.2, 128.7, 128.4, 127.5, 127.0, 126.9, 126.8, 126.7, 126.7, 126.2, 114.9, 113.7, 113.6, 98.7, 55.3, 55.2, 54.1, 54.0, 52.0, 51.6, 46.1, 45.6, 45.0, 38.0, 37.5, 35.3, 31.8, 28.4, 27.1. **IR:** 2951 (w), 1746 (m), 1711 (m), 1651 (m), 1611 (m), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{24}O_4$ 352.1675; Found 352.1677.

Methyl 4''-fluoro-6'-hydroxy-4-methoxy-1'-methyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7ca): Prepared following the general procedure using cyclopropane **5c** (100 mg, 0.38 mmol), anisole (0.41 mL, 3.81 mmol), and $SnCl_4$ (9 μL, 0.08 mmol) in CH_2Cl_2 (3.8 mL) stirred at room temperature for 1.5 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.33), cyclohexenol **7ca** was given as a colorless oil (79 mg, 56% yield). *Complex mixture of keto-enol tautomers and diastereomers*. ^{1}H NMR (500MHz, $CDCl_3$) δ = 12.60 (s, 0.96 H), 12.38 (s, 0.10 H), 7.82 - 7.79 (m, 0.25 H), 7.37 - 7.33 (m, 0.28 H), 7.29 - 7.18 (m, 3.63 H), 7.17 - 7.15 (m, 0.57 H), 7.09 - 7.04 (m, 2.31 H), 7.04 - 6.96 (m, 1.31 H), 6.96 - 6.91 (m, 2.17 H), 6.90 - 6.84 (m, 2.32 H), 3.84 (s, 0.90 H), 3.81 - 3.80 (m, 6.53 H), 3.79 - 3.77 (m, 1.39 H), 3.28 - 3.20 (m, 0.39 H), 3.07 - 2.99 (m, 0.12 H), 2.80 - 2.73 (m, 0.43 H), 2.69 - 2.59 (m, 2.13 H), 2.45 (s, 0.39 H), 2.42 - 2.35 (m, 0.20 H), 2.35 - 2.26 (m, 1.36 H), 2.24 - 2.18 (m, 0.30 H), 2.13 - 2.08 (m, 1.09 H), 2.06 - 1.98 (m, 1.35 H), 1.77 (s, 0.33 H), 1.61 (s, 3.00 H), 1.29 (s, 0.75 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 208.1, 176.4, 174.9, 173.3, 170.4, 161.3 (d, 1JC-F = 244.0 Hz), 160.7, 158.6, 158.0, 157.9, 144.6, 141.1, 141.1, 139.3, 138.8, 138.0, 134.1, 129.8, 128.2, 128.1, 128.1, 128.1, 128.1, 127.8, 127.5, 127.3, 126.9, 115.6, 115.4, 115.2, 115.1, 115.1, 115.0, 114.9, 113.8, 113.6, 98.6, 97.9, 66.8, 55.3, 55.2, 54.0, 54.0, 52.1, 51.7, 48.4, 46.3, 45.7,

45.0, 45.0, 37.7, 37.3, 36.5, 34.6, 32.0, 31.9, 28.4, 27.0, 24.2, 21.6, 14.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -117.21 (quin, J = 6.0 Hz, 0.29 F), -118.01 - -118.07 (m, 0.14 F), -118.26 (quin, J = 6.0 Hz, 1.00 F). **IR:** 2928 (w), 1744 (w), 1715 (w), 1670 (s), 1653 (s), 1508 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{23}O_4F$ 370.1580; Found 370.1570.

Methyl 6'-hydroxy-4-methoxy-1',3'-dimethyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7da): Prepared following the general procedure using cyclopropane **5d** (98 mg, 0.39 mmol), anisole (0.42 mL, 3.87 mmol), and $SnCl_4$ (9 μL, 0.08 mmol) in CH_2Cl_2 (3.9 mL) stirred at room temperature for 1 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.38), cyclohexenol **7da** was given as a colorless oil (61 mg, 44% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.53 (s, 0.90 H), 12.45 (s, 0.44 H), 7.34 - 7.28 (m, 2.35 H), 7.25 - 7.18 (m, 1.91 H), 7.02 - 6.93 (m, 5.09 H), 6.88 - 6.84 (m, 1.03 H), 6.78 - 6.73 (m, 2.07 H), 6.52 - 6.48 (m, 2.00 H), 3.92 - 3.89 (m, 4.31 H), 3.87 - 3.82 (m, 0.98 H), 3.79 (s, 1.41 H), 3.70 (s, 2.90 H), 3.11 (dd, *J* = 2.3, 16.3 Hz, 0.50 H), 3.04 (dd, *J* = 1.8, 16.2 Hz, 1.00 H), 2.51 - 2.43 (m, 2.50 H), 2.32 - 2.27 (m, 0.57 H), 2.23 - 2.18 (m, 0.50 H), 2.08 (d, *J* = 14.0 Hz, 0.97 H), 1.63 (s, 2.96 H), 1.30 - 1.25 (m, 3.70 H), 1.20 (s, 1.45 H), 1.03 (s, 1.45 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 175.9, 175.7, 173.3, 173.1, 157.7, 156.9, 146.1, 140.3, 138.4, 128.2, 127.6, 127.2, 127.2, 126.3, 126.0, 125.9, 125.3, 113.6, 113.1, 97.7, 97.3, 55.2, 53.8, 52.7, 51.9, 51.8, 44.2, 43.9, 36.9, 36.5, 34.4, 34.2, 32.1, 31.9, 28.3, 25.3. **IR:** 2953 (w), 1653 (s), 1612 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{23}H_{26}O_4$ 366.1831; Found 366.1815.

Methyl 2-hydroxy-4'-methoxy-1-methyl-5-(naphthalen-2-yl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (7ea): Prepared following the general procedure using cyclopropane **5e** (100 mg, 0.35 mmol), anisole (0.38 mL, 3.52 mmol), and $SnCl_4$ (8 μL, 0.07 mmol) in CH_2Cl_2 (3.5 mL) stirred at room temperature for 1 h. After work-up and purification (10%

EtOAc/Hexanes, R_f = 0.36), cyclohexenol **7ea** was given as a colorless oil (76 mg, 54% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.65 (s, 1.40 H), 12.42 (s, 0.21 H), 7.87 - 7.67 (m, 10.44 H), 7.56 (br. s., 1.50 H), 7.52 - 7.39 (m, 7.51 H), 7.34 - 7.29 (m, 3.62 H), 7.27 - 7.25 (m, 2.26 H), 7.24 - 7.21 (m, 1.93 H), 7.04 - 7.00 (m, 1.90 H), 6.93 - 6.87 (m, 3.60 H), 3.86 (s, 3.13 H), 3.83 - 3.81 (m, 10.12 H), 3.81 - 3.80 (m, 3.45 H), 3.43 (tt, *J* = 3.3, 12.7 Hz, 1.00 H), 2.89 (dt, *J* = 3.2, 14.6 Hz, 1.26 H), 2.86 - 2.74 (m, 3.24 H), 2.57 - 2.43 (m, 2.93 H), 2.37 - 2.29 (m, 1.27 H), 2.27 - 2.22 (m, 1.56 H), 2.20 - 2.13 (m, 2.51 H), 1.83 (s, 0.71 H), 1.65 (s, 4.45 H), 1.41 (s, 0.42 H), 1.33 (s, 2.82 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 208.3, 175.0, 173.4, 173.1, 170.5, 158.6, 157.9, 142.9, 142.5, 141.0, 138.1, 134.2, 133.5, 133.5, 132.5, 132.2, 128.4, 127.9, 127.6, 127.6, 127.5, 127.5, 127.4, 127.0, 126.2, 126.0, 125.9, 125.8, 125.7, 125.7, 125.4, 125.3, 124.8, 124.8, 124.7, 114.9, 113.8, 113.6, 98.7, 55.3, 55.2, 54.1, 54.1, 52.1, 51.7, 46.2, 45.6, 45.1, 45.0, 38.0, 37.4, 37.3, 36.6, 35.4, 31.8, 31.6, 28.4, 27.1. **IR:** 2928 (w), 1744 (m), 1713 (m), 1653 (m), 1611 (m), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{26}H_{26}O_4$ 402.1831; Found 402.1823.

Methyl 2-hydroxy-4'-methoxy-1-methyl-5-(thiophen-2-yl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (7fa): Prepared following the general procedure using cyclopropane **5a** (101 mg, 0.40 mmol), anisole (0.43 mL, 4.00 mmol), and $SnCl_4$ (9 μL, 0.08 mmol) in CH_2Cl_2 (4.0 mL) stirred at room temperature for 1 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.52), cyclohexenol **7fa** was given as a colorless oil (81 mg, 56% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (500MHz, CDCl3) δ = 12.60 (s, 0.96 H), 12.38 (s, 0.15 H), 7.32 - 7.24 (m, 3.42 H), 7.19 (dd, *J* = 1.1, 5.0 Hz, 0.45 H), 7.18 - 7.13 (m, 1.13 H), 7.12 - 7.10 (m, 1.00 H), 6.99 - 6.95 (m, 1.47 H), 6.94 - 6.92 (m, 0.53 H), 6.91 - 6.84 (m, 4.55 H), 6.74 (dt, *J* = 1.1, 3.4 Hz, 1.00 H), 3.83 (s, 1.37 H), 3.82 (s, 3.55 H), 3.80

(s, 4.41 H), 3.78 - 3.77 (m, 1.33 H), 3.58 - 3.51 (m, 0.51 H), 2.99 - 2.90 (m, 1.77 H), 2.82 (ddd, *J* = 1.8, 5.4, 15.9 Hz, 1.14 H), 2.50 - 2.44 (m, 0.33 H), 2.42 - 2.32 (m, 2.08 H), 2.28 (dt, *J* = 2.1, 12.9 Hz, 1.12 H), 2.18 - 2.07 (m, 0.85 H), 2.06 - 2.00 (m, 1.74 H), 1.77 (s, 0.54 H), 1.62 - 1.60 (m, 3.39 H), 1.40 (s, 0.32 H), 1.30 (s, 1.25 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 207.8, 174.8, 173.2, 158.6, 158.0, 149.6, 137.8, 129.4, 127.5, 127.4, 126.9, 126.8, 126.6, 126.5, 123.3, 122.9, 122.7, 122.6, 114.9, 113.8, 113.7, 98.3, 55.3, 55.2, 55.1, 53.9, 53.8, 52.1, 51.7, 47.4, 46.1, 44.9, 38.5, 36.6, 33.4, 32.5, 31.1, 28.3, 26.9. **IR:** 2951 (w), 2931 (w), 1744 (m), 1711 (m), 1653 (s), 1611 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{20}H_{22}O_4S$ 358.1239; Found 358.1236.

Methyl 5-((*tert*-butyldiphenylsilyl)methyl)-2-hydroxy-4'-methoxy-1-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (7ga): Prepared following the general procedure using cyclopropane **5g** (150 mg, 0.36 mmol), anisole (0.39 mL, 3.56 mmol), and $SnCl_4$ (9 µL, 0.07 mmol) in CH_2Cl_2 (3.6 mL) stirred at room temperature for 27 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.62), cyclohexenol **7ga** was given as a colorless oil (109 mg, 57% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.31 (s, 0.44 H), 12.28 - 12.27 (m, 0.03 H), 7.75 - 7.72 (m, 2.06 H), 7.71 - 7.68 (m, 2.08 H), 7.66 - 7.59 (m, 0.94 H), 7.48 - 7.39 (m, 9.69 H), 7.39 - 7.36 (m, 0.93 H), 7.36 - 7.32 (m, 1.45 H), 7.28 - 7.22 (m, 2.65 H), 6.90 - 6.86 (m, 1.10 H), 6.68 – 6.65 (m, 1.05 H), 6.63 - 6.59 (m, 2.01 H), 6.48 - 6.44 (m, 1.91 H), 3.78 (s, 1.61 H), 3.75 - 3.74 (m, 2.93 H), 3.70 - 3.68 (m, 4.50 H), 3.34 (dd, *J* = 5.2, 13.4 Hz, 1.00 H), 2.32 (dt, *J* = 3.4, 14.3 Hz, 1.00 H), 2.21 (ddd, *J* = 2.1, 5.0, 15.8 Hz, 0.59 H), 2.10 - 2.01 (m, 1.17 H), 1.98 - 1.92 (m, 1.23 H), 1.90 - 1.82 (m, 1.37 H), 1.79 - 1.68 (m, 1.66 H), 1.67 - 1.59 (m, 1.23 H), 1.59 - 1.54 (m, 0.50 H), 1.47 - 1.41 (m, 1.43 H), 1.40 (s, 0.67 H), 1.38 (s, 1.59 H), 1.32 (d, *J* = 5.2 Hz, 0.44 H), 1.28 (d, *J* = 4.9 Hz, 0.74 H), 1.23 - 1.19 (m, 1.32 H), 1.18 – 1.15 (m, 0.78 H), 1.13 – 1.12 (m, 0.46 H), 1.08 (s, 0.70 H), 1.07 -

1.04 (m, 2.03 H), 1.02 (s, 4.10 H), 1.00 (s, 8.61 H), 0.91 - 0.89 (m, 4.55 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 208.9, 174.8, 173.2, 170.6, 157.9, 157.5, 138.2, 136.2, 136.1, 136.0, 135.9, 134.8, 134.7, 134.5, 134.1, 133.9, 129.3, 128.8, 128.7, 127.8, 127.7, 127.4, 127.3, 127.3, 126.8, 114.4, 113.3, 98.8, 55.2, 55.1, 53.7, 53.4, 51.9, 51.4, 49.3, 47.3, 44.6, 40.9, 34.0, 28.2, 27.9, 27.8, 27.7, 27.7, 26.6, 25.3, 24.8, 24.7, 23.3, 18.2, 18.0, 17.9, 16.8. **IR:** 2951 (w), 2857 (w), 1746 (s), 1711 (s), 1653 (m), 1611 (m), 1512 (s) cm^{-1}. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{33}H_{41}O_4Si$ 529.2769; Found 529.2757.

Methyl 6'-hydroxy-3,4,4''-trimethoxy-1'-methyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7ab): The general procedure was followed using cyclopropane **5a** (100 mg, 0.364 mmol), 1,2-dimethoxybenzene (0.47 mL, 3.65 mmol), $SnCl_4$ (9 μL, 0.077 mmol) and CH_2Cl_2 (3.65 mL) at room temperature for 1 h. After work-up and purification (10% EtOAc/hexane, R_f = 0.450), cyclohexenol **7ab** was afforded as a yellow oil (108 mg, 72% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 12.62 (s, 1.12 H), 12.40 (s, 0.29 H), 7.21 - 7.14 (m, 3.23 H), 7.07 - 7.01 (m, 3.20 H), 6.96 - 6.78 (m, 15.43 H), 6.69 (d, J = 2.2 Hz, 1 H), 3.92 - 3.85 (m, 19.30 H), 3.81 - 3.75 (m, 19.84 H), 3.30 - 3.17 (m, 1.31 H), 3.07 - 2.94 (m, 0.42 H), 2.82 - 2.56 (m, 4.94 H), 2.44 - 2.28 (m, 2.92 H), 2.28 - 1.95 (m, 6.91 H), 1.78 (s, 1.21 H), 1.61 (s, 4.32 H), 1.31 (s, 3 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 208.4, 174.7, 173.3, 170.4, 158.4, 157.9, 149.6, 148.6, 147.9, 147.4, 139.4, 138.6, 137.6, 137.1, 135.6, 134.7, 127.6, 127.6, 127.5, 119.0, 117.8, 114.1, 113.8, 113.7, 111.8, 110.7, 109.9, 109.2, 98.7, 98.0, 77.4, 76.6, 56.0, 55.9, 55.9, 55.9, 55.8, 55.2, 55.2, 55.2, 54.3, 54.2, 52.0, 51.6, 46.2, 45.9, 45.2, 37.6, 37.3, 36.3, 34.5, 32.0, 28.1, 27.2. **IR:** 3397 (m), 1648 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{24}H_{28}O_6$ 412.1886; Found 412.1887.

Methyl 6'-hydroxy-2,4,4''-trimethoxy-1'-methyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7ac): Prepared following the general procedure using cyclopropane **5a** (77 mg, 0.28 mmol), 1,3-dimethoxybenzene (0.38 mL, 2.80 mmol), and $SnCl_4$ (6 μL, 0.06 mmol) in CH_2Cl_2 (2.8 mL) stirred at room temperature for 1 h. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.44), cyclohexenol **7ac** was given as a colorless oil (102 mg, 88% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.61 - 12.59 (m, 0.06 H), 12.48 (s, 0.21 H), 7.31 (d, *J* = 8.5 Hz, 1.00 H), 7.20 - 7.10 (m, 3.91 H), 6.88 - 6.81 (m, 3.35 H), 6.60 (dd, *J* = 2.4, 8.5 Hz, 1.05 H), 6.51 (d, *J* = 2.7 Hz, 1.03 H), 6.49 - 6.48 (m, 0.59 H), 6.46 – 6.44 (m, 0.39 H), 3.85 (s, 3.01 H), 3.84 (s, 0.81 H), 3.80 - 3.74 (m, 18.10 H), 3.74 - 3.69 (m, 1.86 H), 3.22 – 3.16 (m, 1.29 H), 3.08 - 3.00 (m, 0.28 H), 2.78 - 2.68 (m, 1.36 H), 2.65 - 2.61 (m, 0.24 H), 2.52 - 2.41 (m, 0.80 H), 2.37 - 2.28 (m, 0.74 H), 2.25 (d, *J* = 12.8 Hz, 1.04 H), 2.22 - 2.14 (m, 1.37 H), 1.90 (dd, *J* = 12.8, 14.3 Hz, 1.19 H), 1.84 - 1.79 (m, 0.44 H), 1.75 (s, 0.77 H), 1.70 – 1.66 (m, 0.75 H), 1.63 - 1.61 (m, 0.82 H), 1.40 (s, 0.22 H), 1.30 (s, 0.40 H), 1.27 - 1.23 (m, 3.55 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 209.3, 207.1, 170.8, 170.7, 160.0, 157.3, 137.9, 136.5, 135.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.0, 126.3, 123.8, 114.0, 113.9, 113.7, 104.9, 103.9, 99.9, 98.9, 55.4, 55.4, 55.3, 55.2, 55.2, 55.0, 54.8, 52.9, 52.0, 51.8, 51.4, 47.5, 47.4, 38.8, 37.6, 37.1, 34.9, 25.5, 24.9, 24.6, 23.5. **IR:** 2936 (w), 1742 (s), 1715 (s), 1611 (m), 1584 (m), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{24}H_{28}O_6$ 412.1886; Found 412.1893.

Methyl 4-(diphenylamino)-6'-hydroxy-4''-methoxy-1'-methyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7ad): Prepared following the general procedure using cyclopropane **5a** (100 mg, 0.37 mmol), triphenylamine (895 mg, 3.65 mmol), and $SnCl_4$ (9 μL, 0.07 mmol) in CH_2Cl_2 (3.7 mL) stirred at room temperature for 1 h. After work-up and

purification (10% EtOAc/Hexanes, R_f = 0.36), cyclohexenol **7ad** was given as a colorless oil (135 mg, 71% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.63 (s, 0.88 H), 12.44 (s, 1.28 H), 7.32 - 7.17 (m, 25.33 H), 7.16 - 7.13 (m, 4.86 H), 7.13 - 6.99 (m, 27.85 H), 6.91 - 6.83 (m, 7.00 H), 3.81 (s, 3.50 H), 3.80 (s, 4.33 H), 3.79 (s, 5.27 H), 3.79 (s, 3.75 H), 3.78 (s, 2.73 H), 3.26 (tt, *J* = 3.3, 12.6 Hz, 1.00 H), 3.05 - 2.97 (m, 1.37 H), 2.79 - 2.73 (m, 2.47 H), 2.72 - 2.64 (m, 1.93 H), 2.43 - 2.34 (m, 2.33 H), 2.34 - 2.23 (m, 2.22 H), 2.15 (t, *J* = 13.3 Hz, 2.40 H), 2.07 - 2.01 (m, 1.92 H), 1.96 (dt, *J* = 2.2, 13.3 Hz, 1.46 H), 1.78 (s, 3.93 H), 1.63 (s, 2.95 H), 1.41 (s, 0.47 H), 1.32 (s, 2.88 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 208.3, 176.3, 173.3, 173.2, 158.4, 158.1, 158.0, 147.7, 147.7, 147.4, 146.7, 145.8, 141.0, 140.1, 137.7, 137.2, 135.7, 135.5, 129.3, 129.1, 129.1, 127.7, 127.6, 127.6, 127.2, 127.0, 126.6, 124.7, 124.2, 124.1, 123.6, 123.6, 123.4, 123.2, 122.6, 122.6, 114.0, 113.8, 113.8, 98.8, 98.2, 55.3, 54.2, 54.1, 52.0, 51.6, 48.7, 46.1, 45.8, 45.3, 45.2, 37.7, 37.1, 36.3, 34.4, 32.1, 31.9, 28.4, 27.0, 24.6, 24.3. **IR:** 2930 (w), 1746 (w), 1713 (w), 1653 (m), 1611 (m), 1587 (m), 1508 (s) cm^{-1}. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{34}H_{33}O_4NNa$ 542.2302; Found 542.2291.

Methyl 4-hydroxy-4'-methoxy-5-(4-methoxynaphthalen-1-yl)-5-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (7ae-*enol*): Prepared following the general procedure using cyclopropane **5a** (103 mg, 0.37 mmol), 1-methoxynaphthalene (576 mg, 3.65 mmol), and $SnCl_4$ (9 μL, 0.07 mmol) in CH_2Cl_2 (3.7 mL) stirred at room temperature for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.34), cyclohexenol **7ae-*enol*** was given as a colorless oil (49 mg, 30% yield). *Mixture of diastereomers and some keto-enol tautomers.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.74 - 12.73 (m, 0.04 H), 12.52 (s, 0.91 H), 8.38 (dd, *J* = 1.5, 8.2 Hz, 1.10 H), 8.19 (d, *J* = 7.9 Hz, 0.98 H), 7.68 - 7.64 (m, 0.08 H), 7.61 - 7.59 (m, 0.21 H), 7.57 (d, *J* = 8.2 Hz, 1.01 H), 7.54 - 7.44 (m, 2.36 H), 7.41 - 7.38 (m, 0.10 H), 7.33 - 7.30 (m, 0.07 H), 7.21

- 7.17 (m, 2.20 H), 7.00 - 6.96 (m, 0.12 H), 6.94 - 6.90 (m, 0.19 H), 6.85 - 6.79 (m, 3.24 H), 6.77 - 6.74 (m, 0.23 H), 4.07 (s, 0.20 H), 4.00 (s, 3.23 H), 3.99 (s, 0.26 H), 3.84 (s, 0.30 H), 3.83 (s, 0.26 H), 3.82 - 3.80 (m, 3.18 H), 3.78 - 3.76 (m, 3.17 H), 3.74 (s, 0.12 H), 3.67 (s, 0.16 H), 3.47 - 3.39 (m, 0.11 H), 3.32 - 3.23 (m, 1.00 H), 3.00 (ddd, J = 2.1, 5.0, 16.1 Hz, 1.10 H), 2.89 - 2.82 (m, 0.18 H), 2.78 (t, J = 13.4 Hz, 1.03 H), 2.62 (dd, J = 11.9, 16.2 Hz, 1.05 H), 2.55 - 2.48 (m, 0.10 H), 2.01 (s, 3.12 H), 1.97 (s, 0.16 H), 1.92 (s, 0.29 H), 1.83 (td, J = 2.4, 13.7 Hz, 1.02 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 178.6, 173.0, 158.1, 154.9, 137.3, 133.0, 131.7, 127.7, 126.6, 126.4, 124.7, 124.5, 124.1, 123.1, 114.0, 113.8, 102.9, 95.8, 55.4, 55.2, 51.7, 45.0, 44.6, 36.3, 31.5, 28.0. **IR:** 1647 (m), 1611 (m), 1514 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{27}H_{28}O_5$ 432.1937; Found 432.1920.

Methyl 3-(4-methoxynaphthalen-1-yl)-5-(4-methoxyphenyl)-3-methyl-2-oxocyclohexane-1-carboxylate (7ae-*keto*): Prepared following the general procedure using cyclopropane **5a** (103 mg, 0.37 mmol), 1-methoxynaphthalene (576 mg, 3.65 mmol), and $SnCl_4$ (9 μL, 0.07 mmol) in CH_2Cl_2 (3.7 mL) stirred at room temperature for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.21), cyclohexanone **7ae-*keto*** was given as a colorless oil (64 mg, 40% yield). *Mixture of diastereomers and some keto-enol tautomers.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.73 (s, 0.07 H), 12.52 (s, 0.03 H), 8.41 - 8.37 (m, 1.02 H), 8.34 - 8.29 (m, 0.10 H), 7.90 - 7.85 (m, 0.99 H), 7.66 (d, J = 8.2 Hz, 1.00 H), 7.58 - 7.55 (m, 0.09 H), 7.54 - 7.49 (m, 2.04 H), 7.49 - 7.41 (m, 0.26 H), 7.35 - 7.29 (m, 0.17 H), 7.27 - 7.22 (m, 2.18 H), 7.20 - 7.16 (m, 0.09 H), 6.99 - 6.95 (m, 0.23 H), 6.94 - 6.88 (m, 2.99 H), 6.76 - 6.73 (m, 0.23 H), 4.06 (s, 2.93 H), 4.00 (s, 0.35 H), 3.83 (s, 0.41 H), 3.82 (s, 2.82 H), 3.81 (s, 0.15 H), 3.77 (s, 0.15 H), 3.73 (s, 0.23 H), 3.66 (s, 2.92 H), 3.58 - 3.49 (m, 2.00 H), 3.01 (td, J = 3.1, 14.8 Hz, 1.00 H), 2.31 (q, J = 12.9 Hz, 1.04 H), 2.25 - 2.17 (m, 1.08 H), 2.09 (dd, J = 13.0, 14.8 Hz, 1.08 H), 1.97 (s, 0.21 H), 1.55 (s, 2.90 H).

^{13}C NMR (126MHz, $CDCl_3$) δ = 213.5, 173.6, 170.1, 158.4, 155.1, 137.7, 135.2, 132.2, 131.4, 129.4, 128.0, 127.7, 127.6, 127.2, 126.7, 125.6, 125.4, 125.2, 124.3, 124.2, 123.6, 122.9, 114.1, 113.8, 113.6, 103.1, 102.6, 55.5, 55.4, 55.3, 55.3, 55.2, 53.9, 51.9, 49.3, 47.3, 39.1, 36.8, 36.3, 31.6, 27.0, 26.0. **IR:** 1744 (m), 1707 (m), 1514 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{27}H_{28}O_5$ 432.1937; Found 432.1918.

Methyl 6'-hydroxy-2,4''-dimethoxy-1',5-dimethyl-1',2',3',4'-tetrahydro-[1,1':3',1''-terphenyl]-5'-carboxylate (7af): Prepared following the general procedure using cyclopropane **5a** (102 mg, 0.37 mmol), 4-methylanisole (0.46 mL, 3.65 mmol), and $SnCl_4$ (9 μL, 0.07 mmol) in CH_2Cl_2 (3.7 mL) stirred at room temperature for 3.5 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.10), cyclohexenol **7af** was given as a colorless oil (22 mg, 15% yield). *Complex mixture of keto-enol tautomers and diastereomers.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.62 (s, 0.10 H), 12.50 (s, 0.76 H), 7.23 - 7.22 (m, 0.22 H), 7.20 - 7.16 (m, 5.20 H), 7.14 (d, *J* = 2.7 Hz, 1.03 H), 7.07 - 7.01 (m, 3.10 H), 6.90 - 6.86 (m, 1.09 H), 6.86 - 6.82 (m, 4.29 H), 6.82 - 6.77 (m, 2.35 H), 3.83 (s, 2.65 H), 3.81 - 3.80 (m, 2.04 H), 3.79 - 3.77 (m, 10.14 H), 3.77 - 3.75 (m, 4.87 H), 3.74 (s, 2.70 H), 3.18 (tt, *J* = 3.3, 12.7 Hz, 1.17 H), 3.09 - 3.02 (m, 0.93 H), 2.79 - 2.72 (m, 1.30 H), 2.66 (1, *J* = 12.8 Hz, 1.08 H), 2.48 (q, *J* = 13.3 Hz, 2.21 H), 2.42 - 2.39 (m, 0.29 H), 2.38 (s, 0.90 H), 2.35 (d, *J* = 3.4 Hz, 0.57 H), 2.33 - 2.31 (m, 3.03 H), 2.30 - 2.25 (m, 4.76 H), 1.94 - 1.90 (m, 0.58 H), 1.88 - 1.86 (m, 0.30 H), 1.83 (dt, *J* = 3.4, 13.4 Hz, 1.17 H), 1.78 (s, 2.69 H), 1.72 (s, 0.36 H), 1.70 (dt, *J* = 2.4, 13.1 Hz, 1.08 H), 1.65 (s, 3.01 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 206.8, 178.6, 173.5, 170.8, 158.0, 153.3, 136.5, 134.6, 134.5, 129.9, 128.3, 128.3, 127.9, 127.7, 127.6, 127.6, 126.8, 113.9, 113.7, 112.2, 111.7, 95.0, 55.7, 55.3, 55.3, 55.2, 54.7, 52.0, 51.4, 50.9, 47.4, 43.8, 43.6, 37.7, 36.2, 34.8, 31.5, 25.5, 23.4, 20.9, 20.8. **IR:** 2951

(w), 1744 (s), 1709 (s), 1647 (m), 1611 (m), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{24}H_{28}O_5$ 396.1937; Found 396.1929.

Methyl 5-(furan-2-yl)-4-hydroxy-4'-methoxy-5-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11aa): The general procedure was followed using cyclopropane **5a** (100 mg, 0.364 mmol), furan **10a** (0.27 mL, 3.72 mmol), $SnCl_4$ (9 μL, 0.077 mmol) and CH_2Cl_2 (3.65 mL) at room temperature for 1.5 h. After work-up and purification (15% EtOAc/hexane, R_f= 0.650), cyclohexenol **11aa** was afforded as a yellow oil (82.3 mg, 66% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 12.56 (s, 0.85 H), 12.43 (s, 0.61 H), 7.47 (dd, *J* = 0.8, 1.8 Hz, 0.33 H), 7.43 (dd, *J* = 0.9, 1.9 Hz, 0.09 H), 7.41 (dd, *J* = 0.9, 1.9 Hz, 0.67 H), 7.37 (dd, *J* = 0.9, 1.9 Hz, 0.89 H), 7.25 - 7.20 (m, 2.32 H), 7.17 - 7.13 (m, 1.95 H), 6.93 - 6.90 (m, 1.80 H), 6.90 - 6.85 (m, 2.81 H), 6.45 (dd, *J* = 1.9, 3.4 Hz, 0.35 H), 6.37 (dd, *J* = 1.9, 3.1 Hz, 0.72 H), 6.35 (dd, *J* = 1.8, 3.3 Hz, 1 H), 6.29 (dd, *J* = 0.8, 3.3 Hz, 0.72 H), 6.26 (dd, *J* = 0.8, 3.3 Hz, 0.37 H), 6.24 (dd, *J* = 0.9, 3.4 Hz, 0.08 H), 6.20 (dd, *J* = 0.8, 3.3 Hz, 0.92 H), 3.83 (s, 1.56 H), 3.83 (s, 2.27 H), 3.82 (s, 3 H), 3.80 (s, 3.92 H), 3.78 (s, 1.98 H), 3.42 - 3.32 (m, 0.50 H), 3.07 - 2.98 (m, 0.74 H), 2.95 - 2.86 (m, 1 H), 2.76 (dd, *J* = 2.3, 4.8 Hz, 0.34 H), 2.74 - 2.70 (m, 1.13 H), 2.68 (dd, *J* = 2.1, 5.1 Hz, 0.75 H), 2.54 - 2.26 (m, 4.63 H), 2.05 - 1.86 (m, 2.44 H), 1.75 (s, 2.21 H), 1.64 (s, 3 H), 1.40 (s, 1.15 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.3, 173.3, 173.1, 172.5, 170.3, 158.4, 158.2, 158.1, 158.0, 155.8, 142.2, 141.4, 141.2, 137.4, 137.1, 127.7, 127.6, 127.6, 114.0, 114.0, 114.0, 113.8, 113.8, 110.6, 110.0, 110.0, 106.0, 105.8, 98.2, 97.6, 77.3, 76.7, 55.2, 54.4, 52.1, 51.6, 51.1, 46.5, 43.5, 42.7, 42.4, 42.4, 37.5, 37.1, 35.6, 35.3, 31.7, 24.9, 24.6, 24.5, 23.5. **IR:** 2941 (w), 1611 (w) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{20}H_{22}O_5$ 342.1467; Found 342.1467.

Methyl 4-hydroxy-4'-methoxy-5-methyl-5-(thiophen-2-yl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11ab): The general procedure was followed using cyclopropane **5a** (100 mg, 0.364 mmol), thiophene **10b** (0.3 mL, 3.75 mmol), $SnCl_4$ (9 µL, 0.077 mmol) and CH_2Cl_2 (3.65 mL) at room temperature for 1 h. After work-up and purification by prepTLC (10% EtOAc/hexane, R_f= 0.450), cyclohexenol **11ab** was afforded as a yellow oil (96.6 mg, 74% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 12.67 (s, 0.18 H), 12.64 (s, 1 H), 12.51 (s, 0.17 H), 12.33 (s, 0.07 H), 7.44 (dd, *J* = 3.0, 5.0 Hz, 0.09 H), 7.35 - 7.32 (m, 0.33 H), 7.31 - 7.29 (m, *J* = 3.3 Hz, 0.21 H), 7.26 - 7.20 (m, 2.66 H), 7.17 - 7.10 (m, 3.22 H), 7.08 - 7.04 (m, 0.55 H), 7.01 (dd, *J* = 1.3, 3.8 Hz, 1.20 H), 6.98 - 6.94 (m, 1.12 H), 6.94 - 6.83 (m, 4.76 H), 3.97 (dd, *J* = 5.5, 13.3 Hz, 0.40 H), 3.84 - 3.78 (m, 12.65 H), 3.48 - 3.39 (m, 0.50 H), 2.96 - 2.87 (m, 1.10 H), 2.79 - 2.64 (m, 2.37 H), 2.45 - 2.20 (m, 4.26 H), 2.18 - 2.03 (m, 2 H), 1.88 (s, 0.31 H), 1.86 (s, 0.56 H), 1.71 (s, 3 H), 1.64 (s, 0.33 H), 1.62 (s, 0.61 H), 1.45 (s, 1 H), 1.35 (s, 0.27 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 205.8, 174.6, 174.4, 173.4, 173.3, 170.4, 158.1, 150.7, 147.6, 147.0, 137.5, 137.3, 135.4, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 126.4, 126.3, 126.1, 124.4, 124.4, 124.3, 123.9, 123.6, 123.5, 114.1, 113.9, 113.9, 113.8, 97.9, 97.8, 97.2, 77.3, 76.7, 55.3, 55.2, 53.9, 52.4, 51.7, 48.9, 47.9, 46.6, 45.5, 43.9, 43.5, 37.4, 36.8, 36.2, 34.9, 31.9, 31.6, 29.0, 28.9, 27.4, 26.7. **IR:** 2929 (w), 1745 (w), 1649 (m), 1610 (m) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{20}H_{22}O_4S$ 358.1239; Found 358.1237.

Methyl 4-hydroxy-4'-methoxy-5-(2-methoxythiophen-3-yl)-5-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11ac): The general procedure was followed using cyclopropane **5a** (100 mg, 0.364 mmol), 2-methoxythiophene **10c** (0.37 mL, 3.67 mmol), $SnCl_4$ (9 µL, 0.077 mmol) and CH_2Cl_2 (3.65 mL) at room temperature for 1.5 h. After work-up and purification (10% EtOAc/hexane, R_f= 0.547), cyclohexenol **11ac** was afforded as a yellow oil (106 mg, 75%

yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 12.61 (s, 0.91 H), 12.50 (s, 0.77 H), 12.32 (s, 0.29 H), 7.24 - 7.14 (m, 5.67 H), 6.93 - 6.85 (m, 5.86 H), 6.81 (d, *J* = 4.0 Hz, 0.18 H), 6.64 (d, *J* = 3.8 Hz, 0.86 H), 6.57 - 6.55 (m, 1.27 H), 6.55 - 6.53 (m, 0.13 H), 6.51 - 6.50 (m, 0.17 H), 6.49 (d, *J* = 4.0 Hz, 0.17 H), 6.44 (d, *J* = 3.8 Hz, 0.28 H), 6.11 - 6.07 (m, 0.51 H), 6.07 - 6.04 (m, 1.21 H), 6.04 - 6.02 (m, 1.22 H), 5.96 (d, *J* = 4.0 Hz, 0.16 H), 4.08 - 4.02 (m, 0.42 H), 4.02 - 3.98 (m, 0.27 H), 3.92 (s, 0.81 H), 3.90 - 3.89 (m, 1.28 H), 3.88 (s, 6.67 H), 3.86 (s, 0.58 H), 3.84 - 3.82 (m, 5.21 H), 3.81 (s, 3.48 H), 3.81 - 3.79 (m, 5.24 H), 3.79 (s, 2.70 H), 3.04 - 2.88 (m, 2.61 H), 2.80 - 2.68 (m, 2.40 H), 2.65 (dd, *J* = 1.9, 5.1 Hz, 0.65 H), 2.55 (td, *J* = 3.3, 14.3 Hz, 0.38 H), 2.44 - 2.27 (m, 4.66 H), 2.22 - 2.16 (m, 1.44 H), 2.11 - 2.05 (m, 1.26 H), 2.04 (s, 0.31 H), 2.01 (s, 0.49 H), 1.97 (s, 0.21 H), 1.88 (s, 1 H), 1.77 (s, 2.51 H), 1.64 (s, 3 H), 1.41 (s, 0.70 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.3, 173.2, 173.1, 172.9, 164.9, 164.5, 158.1, 158.0, 137.3, 137.0, 136.8, 136.3, 127.8, 127.7, 127.6, 121.4, 121.1, 114.0, 113.9, 113.9, 113.8, 102.6, 97.9, 97.2, 77.3, 76.7, 60.2, 60.2, 60.1, 60.0, 59.9, 55.3, 55.2, 53.8, 52.4, 51.7, 47.9, 47.3, 47.2, 46.1, 43.8, 43.6, 39.7, 36.1, 35.0, 34.9, 31.8, 31.6, 31.3, 28.6, 26.0. **IR:** 2991 (w), 1735 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{21}H_{24}O_5S$ 388.1344; Found 388.1339.

Methyl 5-(2,5-dimethylfuran-3-yl)-4-hydroxy-4'-methoxy-5-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11ad): The general procedure was followed using cyclopropane **5a** (100 mg, 0.364 mmol), 2,5-dimethylfuran **10d** (0.39 mL, 3.66 mmol), $InCl_3$ (9 mg, 0.041 mmol) and CH_2Cl_2 (3.65 mL) at room temperature for 24 h. After work-up and purification (10% EtOAc/hexane, R_f = 0.590), cyclohexenol **11ad** was afforded as a yellow oil (61.9 mg, 46% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 12.56 (s, 0.61 H), 12.48 (s, 0.49 H), 7.20 - 7.14 (m, 2.78 H), 7.12 - 7.07 (m, 2.07 H), 6.90 -

6.80 (m, 5.19 H), 5.91 (s, 0.77 H), 5.80 (s, 1 H), 3.84 - 3.72 (m, 15.96 H), 3.01 - 2.81 (m, 1.34 H), 2.79 - 2.56 (m, 4.08 H), 2.36 - 2.16 (m, 17.81 H), 2.10 - 1.83 (m, 7.47 H), 1.67 (s, 2.89 H), 1.51 (s, 3 H), 1.27 - 1.20 (m, 3.06 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 175.9, 174.8, 173.3, 173.1, 158.1, 158.0, 148.5, 144.6, 144.5, 137.7, 137.2, 136.9, 127.7, 127.7, 127.6, 125.0, 123.9, 116.5, 114.0, 113.8, 113.8, 113.8, 106.6, 106.4, 99.6, 98.0, 97.1, 77.3, 76.7, 55.3, 51.6, 46.0, 45.5, 40.3, 39.9, 39.3, 38.2, 35.7, 35.1, 32.1, 31.9, 31.7, 26.6, 25.7, 13.4, 13.4, 13.2, 13.0. **IR:** 2918 (w), 1653 (m), 1610 (m) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{26}O_5$ 370.1780; Found 370.1773.

Methyl 5-(2,5-dimethylthiophen-3-yl)-4-hydroxy-4'-methoxy-5-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11ae): The general procedure was followed using cyclopropane **5a** (100 mg, 0.364 mmol), 2,5-dimethylthiophene **10e** (0.42 mL, 3.69 mmol), $SnCl_4$ (9 μL, 0.077 mmol) and CH_2Cl_2 (3.65 mL) at room temperature for 1.5 h. After work-up and purification (25% EtOAc/hexane, R_f= 0.810), cyclohexenol **11ae** was afforded as a yellow oil (122.4 mg, 87% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 12.60 (s, 0.11 H), 12.51 (s, 0.02 H), 12.30 (s, 0.02 H), 7.21 - 7.15 (m, 2.14 H), 7.10 - 7.06 (m, 0.40 H), 6.91 - 6.85 (m, 2.14 H), 6.84 - 6.80 (m, 0.49 H), 6.69 (s, 1 H), 6.48 (s, 0.16 H), 3.93 - 3.85 (m, 1 H), 3.80 (s, 3 H), 3.79 - 3.75 (m, 4.66 H), 3.37 - 3.21 (m, 1.12 H), 2.71 - 2.61 (m, 1.42 H), 2.45 (s, 3 H), 2.39 - 2.19 (m, 7.31 H), 1.99 - 1.83 (m, 1.56 H), 1.60 (s, 0.52 H), 1.26 (s, 3 H). **^{13}C NMR** (101MHz, $CDCl_3$) δ = 215.8, 176.1, 175.4, 173.4, 173.0, 158.1, 158.0, 146.0, 141.0, 139.5, 137.8, 137.2, 134.4, 133.9, 130.5, 130.4, 127.7, 127.6, 127.6, 127.4, 126.0, 114.1, 113.8, 113.7, 98.1, 96.9, 77.3, 76.7, 55.3, 51.6, 45.3, 45.2, 44.0, 43.2, 35.7, 35.1, 32.1, 31.7, 27.0, 26.6, 15.2, 15.0, 14.5, 14.1. **IR:** 2928 (w), 1653 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{26}O_4S$ 386.1552; Found 386.1551.

Methyl 5-(benzo[*b*]thiophen-3-yl)-4-hydroxy-4'-methoxy-5-methyl-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11af): The general procedure was followed using cyclopropane **5a** (100 mg, 0.364 mmol), 1-benzothiophene **10f** (0.49 g, 3.65 mmol), $SnCl_4$ (9 μL, 0.077 mmol) and CH_2Cl_2 (3.65 mL) at room temperature for 1 h. After work-up and purification (15% EtOAc/hexane, R_f = 0.540), cyclohexenol **11af** was afforded as a yellow oil (108.7 mg, 73% yield). *Complex mixture of keto-enol tautomers and diastereomers*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 12.75 (s, 0.36 H), 12.45 (s, 0.39 H), 8.04 - 7.99 (m, 0.39 H), 7.96 - 7.82 (m, 2.67 H), 7.75 - 7.69 (m, 1.15 H), 7.53 (s, 0.97 H), 7.44 - 7.31 (m, 4.97 H), 7.30 - 7.18 (m, 4.53 H), 7.04 - 6.99 (m, 0.81 H), 6.97 - 6.90 (m, 2.34 H), 6.89 - 6.83 (m, 1.34 H), 6.82 - 6.77 (m, 0.74 H), 3.87 - 3.83 (m, 6.07 H), 3.81 - 3.80 (m, 2.21 H), 3.77 (s, 1.05 H), 3.74 (s, 2.95 H), 3.63 (dd, *J* = 5.5, 13.1 Hz, 1.89 H), 3.25 - 3.14 (m, 0.51 H), 3.00 - 2.89 (m, 1.57 H), 2.82 - 2.75 (m, 0.47 H), 2.74 - 2.53 (m, 2.04 H), 2.43 - 2.23 (m, 3.16 H), 2.21 - 2.11 (m, 1.29 H), 2.06 (t, *J* = 12.8 Hz, 0.57 H), 2.01 - 1.94 (m, 1.61 H), 1.88 (s, 1.25 H), 1.50 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 209.5, 175.4, 172.9, 170.1, 158.5, 158.1, 141.5, 141.1, 140.5, 137.4, 137.0, 136.8, 136.2, 135.1, 127.7, 127.6, 124.6, 124.5, 124.0, 123.9, 123.7, 123.6, 123.4, 123.2, 123.1, 122.6, 122.5, 122.4, 114.1, 113.8, 113.7, 97.2, 77.3, 76.7, 55.3, 55.2, 55.2, 54.3, 53.0, 52.0, 51.8, 51.7, 48.4, 45.2, 43.6, 43.5, 38.3, 37.1, 36.0, 31.8, 26.2, 25.1. **IR:** 3476 (w) cm^{-1}, 1653 cm^{-1} (s). **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{24}H_{24}O_4S$ 408.1395; Found 408.1393.

Methyl 4-hydroxy-4'-methoxy-5-methyl-5-(1-tosyl-1*H*-indol-3-yl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11ag): Prepared following the general procedure using cyclopropane **5a** (88 mg, 0.32 mmol), *N*-tosylindole **10g** (880 mg, 3.24 mmol), and $SnCl_4$ (8 μL, 0.06 mmol) in CH_2Cl_2 (3.2 mL) stirred at room temperature for 1 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.08), cyclohexenol **11ag** was given as a colorless oil (125 mg, 71% yield).

Complex mixture of keto-enol tautomers and diastereomers. **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.67 (s, 0.95 H), 12.34 (s, 0.55 H), 8.04 - 7.99 (m, 1.55 H), 7.96 (d, *J* = 8.2 Hz, 0.64 H), 7.82 - 7.79 (m, 1.33 H), 7.77 - 7.72 (m, 3.27 H), 7.64 - 7.60 (m, 1.54 H), 7.52 (s, 0.63 H), 7.50 - 7.46 (m, 0.63 H), 7.39 (dd, *J* = 0.9, 7.9 Hz, 0.66 H), 7.37 - 7.33 (m, 1.70 H), 7.30 - 7.25 (m, 3.61 H), 7.23 - 7.17 (m, 6.14 H), 7.17 - 7.13 (m, 1.99 H), 6.99 - 6.95 (m, 0.26 H), 6.94 - 6.90 (m, 3.16 H), 6.88 - 6.85 (m, 0.21 H), 6.85 - 6.81 (m, 1.29 H), 6.79 - 6.74 (m, 2.00 H), 3.84 (s, 2.92 H), 3.83 (s, 1.63 H), 3.79 - 3.78 (m, 2.02 H), 3.78 - 3.77 (m, 1.90 H), 3.76 - 3.74 (m, 3.09 H), 3.71 (s, 1.58 H), 3.55 (dd, *J* = 5.2, 13.4 Hz, 0.58 H), 3.49 - 3.40 (m, 0.73 H), 3.12 - 3.04 (m, 0.64 H), 2.78 (s, 1.25 H), 2.66 - 2.60 (m, 1.05 H), 2.56 - 2.39 (m, 3.61 H), 2.36 (s, 2.07 H), 2.34 - 2.32 (m, 5.37 H), 2.32 - 2.27 (m, 1.21 H), 2.24 - 2.18 (m, 0.71 H), 2.10 (dd, *J* = 12.8, 14.3 Hz, 0.76 H), 2.00 (s, 0.31 H), 1.98 (s, 0.50 H), 1.96 - 1.93 (m, 0.51 H), 1.86 - 1.83 (m, 1.90 H), 1.82 (dt, *J* = 13.4, 2.3 Hz, 0.73 H), 1.72 (s, 3.05 H), 1.48 (s, 0.34 H), 1.41 - 1.38 (m, 1.99 H), 1.28 - 1.24 (m, 1.16 H), 1.22 (s, 0.33 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 208.3, 174.6, 173.7, 173.4, 172.9, 170.1, 158.1, 158.0, 145.3, 144.8, 144.8, 137.2, 136.9, 135.9, 135.6, 135.6, 135.2, 135.1, 134.9, 134.9, 130.0, 129.9, 129.8, 128.8, 128.3, 127.9, 127.7, 127.7, 127.7, 127.6, 126.8, 126.8, 126.7, 125.2, 125.0, 124.4, 124.3, 123.7, 123.6, 123.4, 123.1, 123.0, 122.9, 121.2, 120.3, 120.3, 114.2, 114.1, 113.9, 113.8, 113.8, 113.7, 98.3, 97.5, 55.3, 55.3, 55.2, 54.2, 52.1, 51.8, 51.8, 50.0, 47.3, 44.3, 43.3, 42.1, 41.0, 37.9, 37.3, 36.6, 36.0, 35.1, 31.8, 31.6, 25.6, 25.3, 24.9, 21.6, 21.5. **IR:** 1744 (m), 1715 (m), 1653 (s), 1611 (s), 1514 (s) cm^{-1}. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{31}O_6NSNa$ 568.1764; Found 568.1753.

Methyl 4-hydroxy-4'-methoxy-5-methyl-5-(3-methyl-1-tosyl-1*H*-indol-2-yl)-1,2,5,6-tetrahydro-[1,1'-biphenyl]-3-carboxylate (11ah): Prepared following the general procedure using cyclopropane **5a** (100 mg, 0.37 mmol), *N*-tosyl-3-methylindole **10h** (1.04 g, 3.65 mmol),

and $SnCl_4$ (9 μL, 0.07 mmol) in CH_2Cl_2 (3.6 mL) stirred at room temperature for 1 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.48), cyclohexenol **11ah** was given as a colorless oil (5 mg, trace yield). *Complex mixture of keto-enol tautomers and diastereomers. Could not fully characterize.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 12.55 (s, 0.29 H), 12.32 (s, 0.93 H), 7.62 - 7.54 (m, 2.27 H), 7.50 - 7.47 (m, 0.53 H), 7.37 - 7.31 (m, 1.84 H), 7.24 - 7.14 (m, 8.82 H), 7.13 - 7.07 (m, 2.30 H), 6.97 - 6.94 (m, 1.19 H), 6.93 - 6.89 (m, 1.63 H), 6.85 - 6.81 (m, 2.58 H), 6.77 – 6.75 (m, 0.91 H), 3.85 (s, 1.01 H), 3.82 (s, 2.01 H), 3.81 (s, 3.06 H), 3.78 - 3.77 (m, 3.68 H), 3.75 - 3.73 (m, 3.21 H), 3.58 - 3.50 (m, 1.09 H), 3.17 - 3.09 (m, 1.35 H), 3.03 - 2.96 (m, 0.89 H), 2.93 - 2.81 (m, 2.87 H), 2.75 - 2.69 (m, 0.63 H), 2.57 - 2.50 (m, 1.73 H), 2.46 (s, 0.46 H), 2.39 (d, J = 1.2 Hz, 1.85 H), 2.35 - 2.32 (m, 3.52 H), 2.31 - 2.29 (m, 1.22 H), 2.12 (s, 3.00 H), 2.01 - 1.99 (m, 1.51 H).

Krapcho Decarbalkoxylations.

General Procedure: A flask with a stir bar was charged with sodium chloride (3.0 equiv.) and water (3 drops). The appropriate cyclohexenol was added (1.0 equiv., as a solution in DMF). The volume of DMF used was such that the final concentration of cyclohexenol in DMF was 0.25 M. The reaction apparatus was then evacuated and refilled with nitrogen three times. The reaction was heated to reflux and monitored by TLC until complete conversion of the cyclohexenol was observed. The reaction was quenched with water (1 mL) and extracted three times with Et_2O. The combined organic layers were washed three times with brine, dried over Na_2SO_4, and concentrated under reduced pressure. ^{1}H NMR spectra of the crude mixtures were used to determine diastereomeric ratios. The resulting mixtures were purified by silica gel flash chromatography using EtOAc/hexanes as the eluent.

(2*R*,4*R*)/(2*S*,4*S*)-2,4-Bis(4-methoxyphenyl)-2-methylcyclohexan-1-one (9aa): Prepared according to the general procedure using cyclohexenol **7aa** (104 mg, 0.27 mmol) and NaCl (46 mg, 0.78 mmol) in DMF (1.04 mL) and H_2O (3 drops) heated to reflux for 20 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.48), cyclohexanone **9aa** was given as a colorless oil (55 mg, 63% yield). *(Diastereomeric ratio = 7.7:1) Only major diastereomer isolated.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.20 - 7.13 (m, 4 H), 6.95 - 6.91 (m, 2 H), 6.90 - 6.86 (m, 2 H), 3.82 (s, 3 H), 3.81 (s, 3 H), 3.17 (tt, *J* = 3.2, 12.6 Hz, 3 H), 2.75 (td, *J* = 3.2, 14.4 Hz, 1 H), 2.61 (dt, *J* = 6.0, 14.0 Hz, 1 H), 2.41 - 2.36 (m, 1 H), 2.12 - 2.05 (m, 1 H), 2.00 - 1.87 (m, 2 H), 1.27 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.6, 158.3, 158.2, 136.8, 135.1, 127.5, 126.9, 114.5, 114.0, 55.3, 55.2, 53.4, 45.6, 39.4, 38.3, 35.6, 28.6. **IR:** 2959 (w), 2928 (w), 2836 (w), 1705 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{21}H_{24}O_3$ 324.1725; Found 324.1723.

(2*R*,4*R*)/(2*S*,4*S*)-2-(4-Methoxyphenyl)-2-methyl-4-phenylcyclohexan-1-one (9ba): Prepared according to the general procedure using **7ba** (112 mg, 0.32 mmol) and NaCl (56 mg, 0.95 mmol) in DMF (1.27 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.42), compound **9ba** was given as a colorless oil (54 mg, 58% yield). (*Diastereomeric ratio* = 11.7:1). *Only major diastereomer isolated.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.37 - 7.32 (m, 2 H), 7.28 - 7.23 (m, 3 H), 7.19 - 7.14 (m, 2 H), 6.96 - 6.92 (m, 7 H), 3.83 (s, 3 H), 3.26 - 3.19 (m, 1 H), 2.79 (td, *J* = 3.2, 14.3 Hz, 1 H), 2.63 (dt, *J* = 6.1, 13.9 Hz, 1 H), 2.43 - 2.38 (m, 1 H), 2.15 - 2.09 (m, 1 H), 2.04 - 1.92 (m, 2 H), 1.28 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.5, 158.3, 144.7, 135.1, 128.6, 126.9, 126.7, 126.6, 114.5, 55.3, 53.4, 45.4, 39.3, 39.2, 35.4, 28.6. **IR:** 2961 (w), 2928 (w), 1705 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{20}H_{22}O_2$ 294.1620; Found 294.1625.

(2*R*,4*R*)/(2*S*,4*S*)-4-(4-Fluorophenyl)-2-(4-methoxyphenyl)-2-methylcyclohexan-1-one (9ca): Prepared according to the general procedure using **7ca** (80 mg, 0.21 mmol) and NaCl (38 mg, 0.65 mmol) in DMF (0.86 mL) and H_2O (3 drops) heated to reflux for 2 d. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.49), compound **9ca** was given as a colorless oil (38 mg, 57% yield). (*Diastereomeric ratio* = 10.5:1) *Only major diastereomer isolated.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.23 - 7.19 (m, 2 H), 7.16 - 7.12 (m, 2 H), 7.05 - 6.99 (m, 2 H), 6.95 - 6.91 (m, 2 H), 3.82 (s, 3 H), 3.20 (tt, *J* = 3.3, 12.6 Hz, 1 H), 2.75 (td, *J* = 3.2, 14.3 Hz, 1 H), 2.61 (dt, *J* = 6.1, 14.0 Hz, 1 H), 2.42 - 2.37 (m, 1 H), 2.07 (d, *J* = 3.4 Hz, 1 H), 1.99 - 1.86 (m, 2 H), 1.27 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.3, 161.5 (d, 1JC-F = 243 Hz), 158.3, 140.4, 140.4, 135.0, 128.1, 128.0, 126.9, 115.5, 115.3, 114.6, 55.3, 53.4, 45.5, 39.2, 38.5, 35.6, 28.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -117.69 (quin, J = 6.0 Hz, 1 F). **IR:** 2929 (w), 1705 (s), 1508 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{20}H_{21}O_2F$ 312.1526; Found 312.1522.

2-(4-Methoxyphenyl)-2,4-dimethyl-4-phenylcyclohexan-1-one (9da): Prepared according to the general procedure using cyclohexenol **7da** (61 mg, 0.17 mmol) and NaCl (29 mg, 0.49 mmol) in DMF (0.65 mL) and H_2O (3 drops) heated to reflux for 1 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.29), compound **9da** was given as a colorless oil (31 mg, 61% yield). (*Diastereomeric ratio* = 2.0:1) **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.45 - 7.41 (m, 1 H), 7.38 - 7.33 (m, 1.32 H), 7.26 - 7.22 (m, 2.76 H), 7.22 - 7.15 (m, 3.40 H), 7.12 - 7.08 (m, 1 H), 6.91 - 6.87 (m, 1.15 H), 6.80 - 6.76 (m, 2 H), 6.59 - 6.55 (m, 2 H), 3.81 (s, 1.70 H), 3.69 (s, 3 H), 3.13 (dd, *J* = 1.5, 15.0 Hz, 1 H), 2.90 - 2.83 (m, 1 H), 2.77 (ddd, *J* = 5.6, 7.9, 16.7 Hz, 1 H), 2.62 - 2.55 (m, 1.63 H), 2.44 (dddd, *J* = 1.4, 5.8, 8.4, 14.0 Hz, 1 H), 2.35 (dt, *J* = 4.6, 12.8 Hz, 0.61 H), 2.19 (d, *J* = 14.6 Hz, 1 H), 2.13 - 2.05 (m, 1.66 H), 1.90 - 1.83 (m, 1 H), 1.34 (s, 3 H), 1.30 (s, 3 H), 1.22 (s, 1.70 H), 1.14 (s, 1.69 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 215.2, 214.8,

158.0, 157.7, 149.5, 148.7, 136.8, 134.9, 128.4, 128.0, 127.1, 126.9, 126.0, 125.5, 125.5, 125.1, 113.9, 113.4, 55.2, 55.1, 52.5, 50.5, 50.3, 37.9, 37.8, 37.0, 37.0, 36.6, 33.6, 33.2, 29.5, 29.1, 28.2. **IR:** 2963 (w), 2930 (w), 1705 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{21}H_{24}O_2$ 308.1776; Found 308.1772.

(2*R*,4*R*)/(2*S*,4*S*)-2-(4-Methoxyphenyl)-2-methyl-4-(naphthalen-2-yl)cyclohexan-1-one (9ea): Prepared according to the general procedure using **7ea** (88 mg, 0.22 mmol) and NaCl (39 mg, 0.67 mmol) in DMF (0.90 mL) and H_2O (3 drops) heated to reflux for 2.5 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.32), compound **9ea** was given as a colorless oil (49 mg, 65% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.86 - 7.80 (m, 3 H), 7.70 (s, 1 H), 7.52 - 7.44 (m, 2 H), 7.41 (dd, *J* = 1.5, 8.5 Hz, 1 H), 7.23 - 7.18 (m, 2 H), 7.00 - 6.95 (m, 2 H), 3.85 (s, 3 H), 3.40 (tt, *J* = 3.1, 12.5 Hz, 1 H), 2.88 (td, *J* = 3.2, 14.3 Hz, 1 H), 2.69 (dt, *J* = 6.1, 13.9 Hz, 1 H), 2.46 (ddd, *J* = 2.4, 4.0, 13.7 Hz, 1 H), 2.25 - 2.17 (m, 1 H), 2.17 - 2.02 (m, 2 H), 1.32 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.4, 158.3, 142.1, 135.1, 133.5, 132.3, 128.2, 127.6, 127.5, 127.0, 126.1, 125.5, 125.5, 124.7, 114.6, 55.3, 53.4, 45.3, 39.3, 39.2, 35.3, 28.6. **IR:** 2963 (w), 2928 (w), 2911 (w), 1705 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{24}H_{24}O_2$ 344.1776; Found 344.1768.

(2*S*,4*R*)/(2*R*,4*S*)-2-(4-Methoxyphenyl)-2-methyl-4-(naphthalen-2-yl)cyclohexan-1-one (*epi*-9ea): Prepared according to the general procedure using **7ea** (88 mg, 0.22 mmol) and NaCl (39 mg, 0.67 mmol) in DMF (0.90 mL) and H_2O (3 drops) heated to reflux for 2.5 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.32), compound ***epi*-9ea** was given as a colorless oil (9 mg, 12% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.84 - 7.78 (m, 4 H), 7.70 (s, 1 H), 7.52 - 7.39 (m, 5 H), 7.25 - 7.21 (m, 2 H), 6.91 - 6.87 (m, 3 H), 3.80 (s, 3 H), 3.48 (tt, *J* = 3.7, 12.5 Hz, 1 H), 2.92 (ddd, *J* = 6.4, 13.1, 15.6 Hz, 1 H), 2.65 (ddd, *J* = 2.7, 5.2, 15.6 Hz,

1 H), 2.56 (t, *J* = 13.1 Hz, 1 H), 2.42 - 2.33 (m, 1 H), 2.27 - 2.14 (m, 2 H), 1.76 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.6, 158.1, 142.2, 136.4, 133.5, 132.3, 128.2, 128.2, 127.6, 127.6, 126.1, 125.6, 125.5, 124.8, 113.5, 55.2, 52.9, 48.6, 39.0, 38.4, 33.3, 24.4. **IR:** 2970 (w), 2932 (w), 1707 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{24}H_{24}O_2$ 344.1776; Found 344.1774.

(2*R*,4*R*)/(2*S*,4*S*)-2-(4-Methoxyphenyl)-2-methyl-4-(thiophen-2-yl)cyclohexan-1-one (9fa): Prepared according to the general procedure using **7fa** (74 mg, 0.21 mmol) and NaCl (37 mg, 0.63 mmol) in DMF (0.84 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.41), compound **9fa** was given as a colorless oil (41 mg, 65% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.18 (dd, *J* = 1.2, 5.2 Hz, 1 H), 7.16 - 7.13 (m, 2 H), 6.97 (dd, *J* = 3.5, 5.0 Hz, 1 H), 6.94 - 6.91 (m, 2 H), 6.88 (td, *J* = 1.0, 3.4 Hz, 1 H), 3.82 (s, 3 H), 3.51 (tt, *J* = 3.2, 12.3 Hz, 1 H), 2.95 (td, *J* = 3.2, 14.3 Hz, 1 H), 2.61 (dt, *J* = 6.1, 14.0 Hz, 1 H), 2.41 - 2.36 (m, 1 H), 2.30 - 2.24 (m, 1 H), 2.04 - 1.89 (m, 2 H), 1.28 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 212.9, 158.3, 134.7, 126.8 (2), 126.7, 123.0, 122.6, 114.6, 55.3, 53.2, 46.0, 39.0, 36.4, 34.5, 28.5. **IR:** 2961 (w), 2926 (w), 2859 (w), 1707 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{18}H_{20}O_2S$ 300.1184; Found 300.1172.

(2*S*,4*R*)/(2*R*,4*S*)-2-(4-Methoxyphenyl)-2-methyl-4-(thiophen-2-yl)cyclohexan-1-one (*epi*-9fa): Prepared according to the general procedure using **7fa** (74 mg, 0.21 mmol) and NaCl (37 mg, 0.63 mmol) in DMF (0.84 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.21), compound ***epi*-9fa** was given as a colorless oil (7 mg, 11% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.22 - 7.18 (m, 2 H), 7.16 (dd, *J* = 1.2, 4.9 Hz, 1 H), 6.95 (dd, *J* = 3.4, 5.2 Hz, 1 H), 6.90 - 6.86 (m, 3 H), 3.81 - 3.79 (m, 3 H), 3.62 (tt, *J* = 3.6, 12.1 Hz, 1 H), 2.87 (ddd, *J* = 6.3, 13.2, 15.6 Hz, 1 H), 2.59 (ddd, *J* =

2.9, 5.0, 15.6 Hz, 1 H), 2.49 - 2.41 (m, 2 H), 2.31 (td, *J* = 3.4, 13.7 Hz, 1 H), 2.12 - 2.03 (m, 1 H), 1.70 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.1, 158.2, 148.7, 136.0, 128.1, 126.7, 123.0, 122.7, 113.5, 55.2, 52.8, 49.3, 38.0, 34.5, 34.3, 24.2. **IR:** 2926 (w), 1707 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{18}H_{20}O_2S$ 300.1184; Found 300.1184.

(2*R*,4*R*)/(2*S*,4*S*)-4-((*tert*-Butyldiphenylsilyl)methyl)-2-(4-methoxyphenyl)-2-methylcyclohexan-1-one (9ga): Prepared according to the general procedure using **7ga** (109 mg, 0.21 mmol) and NaCl (36 mg, 0.62 mmol) in DMF (0.83 mL) and H_2O (3 drops) heated to reflux for 4 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.44), compound **9ga** was given as a colorless oil (66 mg, 68% yield). (*Diastereomeric ratio* = 11.2:1) *Only major diastereomer isolated.* **^{1}H NMR** (500MHx, $CDCl_3$) δ = 7.75 - 7.71 (m, 2 H), 7.71 - 7.68 (m, 2 H), 7.47 - 7.37 (m, 6 H), 6.63 - 6.59 (m, 2 H), 6.57 - 6.53 (m, 2 H), 3.74 (s, 3 H), 2.36 (d, *J* = 14.3 Hz, 1 H), 2.20 - 2.12 (m, 1 H), 2.10 - 2.01 (m, 2 H), 1.79 - 1.72 (m, 1 H), 1.42 (dd, *J* = 12.4, 14.5 Hz, 2 H), 1.22 (dd, *J* = 2.7, 6.4 Hz, 2 H), 1.03 (s, 3 H), 1.02 - 0.99 (m, 9 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 214.3, 157.8, 152.4, 136.1, 136.1, 136.1, 136.0, 135.1, 134.6, 134.4, 129.2, 129.2, 127.7, 127.6, 126.8, 114.0, 60.4, 55.1, 52.9, 47.9, 39.1, 38.4, 32.5, 29.1, 28.5, 27.7, 21.0, 18.2, 17.2, 15.8, 14.2. **IR:** 2961 (w), 2928 (w), 2857 (w), 1705 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{31}H_{38}O_2Si$ 470.2641; Found 470.2646.

(2*R*,4*R*)/(2*S*,4*S*)-2-(3,4-Dimethoxyphenyl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (9ab): Prepared according to the general procedure using **7ab** (125 mg, 0.30 mmol) and NaCl (53 mg, 0.91 mmol) in DMF (1.2 mL) and H_2O (3 drops) heated to reflux for 3.5 h. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.38), compound **9ab** was given as a colorless oil (77 mg, 72% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.19 - 7.15 (m, 2 H), 6.91 - 6.86 (m, 3 H), 6.82 (dd, *J* = 2.1, 8.2 Hz, 1 H), 6.70 (d, *J* = 2.1 Hz, 1 H), 3.89 (s, 3 H), 3.87

(s, 3 H), 3.80 (s, 3 H), 3.22 (tt, *J* = 3.2, 12.5 Hz, 1 H), 2.73 (td, *J* = 3.2, 14.4 Hz, 1 H), 2.61 (dt, *J* = 6.1, 14.0 Hz, 1 H), 2.39 (ddd, *J* = 2.4, 4.0, 13.7 Hz, 1 H), 2.11 - 2.05 (m, *J* = 3.4 Hz, 1 H), 2.00 - 1.86 (m, 2 H), 1.28 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.5, 158.2, 149.4, 147.8, 136.8, 135.5, 127.5, 117.9, 114.0, 111.6, 109.2, 55.9, 55.9, 55.3, 53.6, 45.7, 39.4, 38.4, 35.5, 28.5. **IR:** 2963 (w), 2930 (w), 2909 (w), 1705 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{26}O_4$ 354.1831; Found 354.1827.

(2*S*,4*R*)/(2*R*,4*S*)-2-(3,4-Dimethoxyphenyl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (*epi*-9ab): Prepared according to the general procedure using **7ab** (125 mg, 0.30 mmol) and NaCl (53 mg, 0.91 mmol) in DMF (1.2 mL) and H_2O (3 drops) heated to reflux for 3.5 h. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.23), compound ***epi*-9ab** was given as a colorless oil (14 mg, 13% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.22 - 7.18 (m, 2 H), 6.89 - 6.85 (m, 2 H), 6.83 (d, *J* = 1.5 Hz, 2 H), 6.79 - 6.77 (m, 1 H), 3.88 - 3.85 (m, 6 H), 3.80 (s, 3 H), 3.26 (tt, *J* = 3.7, 12.4 Hz, 1 H), 2.85 (ddd, *J* = 6.4, 12.6, 15.5 Hz, 1 H), 2.63 - 2.57 (m, 1 H), 2.42 (t, *J* = 13.1 Hz, 1 H), 2.29 - 2.22 (m, 1 H), 2.14 (dt, *J* = 3.4, 13.7 Hz, 1 H), 2.06 (dq, *J* = 5.5, 12.8 Hz, 1 H), 1.70 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.7, 158.2, 148.4, 147.8, 136.9, 136.8, 127.6, 119.0, 114.0, 111.1, 110.7, 56.0, 55.8, 55.3, 53.1, 48.7, 38.3, 38.0, 33.3, 24.6. **IR**: 2931 (w), 2835 (w), 1703 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{26}O_4$ 354.1831; Found 354.1824.

(2*R*,4*R*)/(2*S*,4*S*)-2-(2,4-Dimethoxyphenyl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (9ac): Prepared according to the general procedure using **7ac** (47 mg, 0.11 mmol) and NaCl (20 mg, 0.34 mmol) in DMF (0.56 mL) and H_2O (3 drops) heated to reflux for 2 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.28), compound **9ac** was given as a colorless oil (30 mg, 74% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.19 - 7.16 (m, 3 H),

6.86 - 6.82 (m, 2 H), 6.50 - 6.46 (m, 2 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.16 - 3.09 (m, 1 H), 2.73 - 2.68 (m, 2 H), 2.42 (t, J = 13.3 Hz, 1 H), 2.18 - 2.12 (m, 2 H), 1.83 - 1.78 (m, 1 H), 1.61 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.2, 159.7, 158.0, 156.4, 137.6, 128.2, 127.5, 126.5, 113.8, 104.0, 100.0, 55.3, 55.3, 55.2, 50.2, 47.3, 38.7, 38.5, 32.2, 23.6. **IR:** 2938 (w), 2835 (w), 1701 (s), 1611 (m), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{26}O_4$ 354.1831; Found 354.1829.

(2*S*,4*R*)/(2*R*,4*S*)-2-(2,4-Dimethoxyphenyl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (*epi*-9ac): Prepared according to the general procedure using **7ac** (47 mg, 0.11 mmol) and NaCl (20 mg, 0.34 mmol) in DMF (0.56 mL) and H_2O (3 drops) heated to reflux for 2 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.42), compound ***epi*-9ac** was given as a colorless oil (6 mg, 15% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.31 (d, J = 8.5 Hz, 1 H), 7.16 - 7.12 (m, 2 H), 6.88 - 6.83 (m, 2 H), 6.59 (dd, J = 2.4, 8.5 Hz, 1 H), 6.48 (d, J = 2.4 Hz, 1 H), 3.84 (s, 3 H), 3.79 (s, 3 H), 3.72 (s, 3 H), 3.17 (tt, J = 3.6, 12.6 Hz, 1 H), 2.71 (td, J = 3.2, 14.3 Hz, 1 H), 2.65 - 2.57 (m, 1 H), 2.29 - 2.24 (m, 1 H), 2.10 - 2.03 (m, 1 H), 1.93 - 1.81 (m, 2 H), 1.24 - 1.21 (m, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 214.8, 159.7, 158.2, 157.7, 136.7, 127.6, 127.1, 125.1, 114.0, 113.9, 105.0, 99.3, 55.4, 55.3, 55.1, 51.7, 47.6, 38.7, 38.4, 37.2, 25.3. **IR:** 2932 (w), 2859 (w), 1713 (s), 1611 (m), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{26}O_4$ 354.1831; Found 354.1838.

(2*R*,4*R*)/(2*S*,4*S*)-2-(4-(Diphenylamino)phenyl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (9ad): Prepared according to the general procedure using **7ad** (139 mg, 0.27 mmol) and NaCl (47 mg, 0.81 mmol) in DMF (1.07 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.40), compound **9ad** was given as a colorless oil (48 mg, 39% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.30 -

7.25 (m, 4 H), 7.20 - 7.16 (m, 2 H), 7.14 - 7.10 (m, 4 H), 7.08 (s, 4 H), 7.06 - 7.02 (m, 2 H), 6.90 - 6.86 (m, 2 H), 3.80 (s, 3 H), 3.22 (tt, *J* = 3.1, 12.6 Hz, 1 H), 2.74 (td, *J* = 3.2, 14.4 Hz, 1 H), 2.67 (dt, *J* = 6.0, 14.0 Hz, 1 H), 2.43 - 2.37 (m, 1 H), 2.16 - 2.09 (m, *J* = 3.4 Hz, 1 H), 1.99 - 1.92 (m, 2 H), 1.29 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.5, 158.2, 147.6, 146.4, 136.8, 136.6, 129.3, 127.5, 126.6, 124.5, 123.7, 123.0, 114.0, 55.3, 53.5, 45.7, 39.5, 38.3, 35.5, 28.6. **IR:** 2963 (w), 2928 (w), 1707 (s), 1589 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{32}H_{31}O_2N$ 461.2355; Found 461.2357.

(2*S*,4*R*)/(2*R*,4*S*)-2-(4-(Diphenylamino)phenyl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (*epi*-9ad): Prepared according to the general procedure using **7ad** (139 mg, 0.27 mmol) and NaCl (47 mg, 0.81 mmol) in DMF (1.07 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.20), compound ***epi*-9ad** was given as a colorless oil (24 mg, 19% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.26 - 7.19 (m, 6 H), 7.15 - 7.12 (m, 2 H), 7.11 - 7.08 (m, 4 H), 7.05 - 6.98 (m, 4 H), 6.89 - 6.86 (m, 2 H), 3.80 (s, 3 H), 3.27 (tt, *J* = 3.6, 12.4 Hz, 1 H), 2.87 (ddd, *J* = 6.4, 12.9, 15.5 Hz, 1 H), 2.64 - 2.58 (m, 1 H), 2.40 (t, *J* = 13.1 Hz, 1 H), 2.29 - 2.22 (m, 1 H), 2.13 (td, *J* = 3.2, 13.7 Hz, 1 H), 2.11 - 2.01 (m, 1 H), 1.71 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.6, 158.2, 147.7, 146.0, 138.4, 136.9, 129.1, 127.8, 127.6, 124.2, 123.3, 122.6, 113.9, 55.3, 53.1, 49.1, 38.4, 38.1, 33.4, 24.3. **IR:** 2932 (w), 1705 (s), 1587 (s), 1510 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{32}H_{31}O_2N$ 461.2355; Found 461.2357.

(2*R*,4*R*)/(2*S*,4*S*)-2-(4-Methoxynaphthalen-1-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (9ae): Prepared according to the general procedure using cyclohexenol **7ae** (113 mg, 0.26 mmol) and NaCl (45 mg, 0.76 mmol) in DMF (1.0 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (15% EtOAc/Hexanes, R_f = 0.42), compound **9ae** was given

as a colorless oil (43 mg, 44% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 8.43 - 8.37 (m, 1 H), 7.96 - 7.91 (m, 1 H), 7.70 (d, *J* = 8.2 Hz, 1 H), 7.53 - 7.48 (m, 2 H), 7.28 - 7.24 (m, 2 H), 6.97 - 6.91 (m, 3 H), 4.09 (s, 3 H), 3.85 (s, 3 H), 3.55 (tt, *J* = 3.7, 12.7 Hz, 1 H), 3.02 (td, *J* = 3.2, 14.6 Hz, 1 H), 2.43 (ddd, *J* = 5.5, 11.4, 13.9 Hz, 1 H), 2.32 - 2.27 (m, 1 H), 2.15 - 1.94 (m, 3 H), 1.57 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 218.7, 154.8, 136.2, 132.6, 130.4, 127.7, 127.1, 126.6, 124.9, 124.2, 123.5, 123.0, 114.0, 103.1, 55.5, 55.3, 54.9, 49.4, 39.9, 38.0, 37.4, 26.3. **IR:** 2932 (w), 1703 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{25}H_{26}O_3$ 374.1882; Found 374.1878.

(2*S*,4*R*)/(2*R*,4*S*)-2-(4-Methoxynaphthalen-1-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (*epi*-9ae): Prepared according to the general procedure using cyclohexenol **7ae** (113 mg, 0.26 mmol) and NaCl (45 mg, 0.76 mmol) in DMF (1.0 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (15% EtOAc/Hexanes, R_f = 0.12), compound ***epi*-9ae** was given as a colorless oil (34 mg, 34% yield). *Minor diastereomer.* ^{1}H NMR (500MHz, $CDCl_3$) δ = 8.38 (td, *J* = 0.8, 8.2 Hz, 1 H), 7.56 - 7.49 (m, 2 H), 7.49 - 7.42 (m, 2 H), 7.22 - 7.16 (m, 2 H), 6.86 - 6.81 (m, 2 H), 6.78 (d, *J* = 8.2 Hz, 1 H), 3.99 (s, 3 H), 3.77 (s, 3 H), 3.40 (tt, *J* = 3.5, 12.6 Hz, 1 H), 3.05 (ddd, *J* = 6.7, 13.8, 17.3 Hz, 1 H), 2.91 - 2.84 (m, 1 H), 2.78 (t, *J* = 13.6 Hz, 1 H), 2.50 - 2.32 (m, 2 H), 2.01 (dt, *J* = 3.4, 13.9 Hz, 1 H), 1.91 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.5, 158.1, 154.9, 136.8, 133.4, 130.4, 127.6, 126.9, 125.8, 125.7, 124.3, 124.2, 123.3, 113.9, 102.9, 55.4, 55.2, 52.8, 48.0, 38.6, 38.5, 32.7, 25.7. **IR:** 2938 (w), 2911 (w), 1703 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{25}H_{26}O_3$ 374.1882; Found 374.1875.

(2*R*,4*R*)/(2*S*,4*S*)-2-(Furan-2-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (12aa): Prepared according to the general procedure using **11aa** (74 mg, 0.18 mmol) and NaCl (27 mg, 0.46 mmol) in DMF (0.61 mL) and H_2O (3 drops) heated to reflux for 2 d. After work-up and

purification (20% EtOAc/Hexanes, R_f = 0.32), compound **12aa** was given as a colorless oil (10 mg, 16% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.39 (dd, *J* = 0.6, 1.8 Hz, 1 H), 7.19 - 7.14 (m, 2 H), 6.90 - 6.84 (m, 2 H), 6.38 (dd, *J* = 1.8, 3.4 Hz, 1 H), 6.16 (dd, *J* = 0.8, 3.2 Hz, 1 H), 3.80 (s, 3 H), 3.27 (tt, *J* = 3.5, 12.6 Hz, 1 H), 2.72 - 2.63 (m, 2 H), 2.48 - 2.42 (m, 1 H), 2.17 - 2.09 (m, 1 H), 1.96 - 1.85 (m, 2 H), 1.34 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 210.0, 158.2, 156.8, 141.8, 136.6, 127.6, 114.0, 110.5, 105.4, 55.3, 50.6, 46.4, 39.4, 38.7, 34.8, 24.7. **IR:** 2928 (w), 1712 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{18}H_{20}O_3$ 284.1412; Found 284.1405.

(2*S*,4*R*)/(2*R*,4*S*)-2-(Furan-2-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (*epi*-12aa): Prepared according to the general procedure using **11aa** (74 mg, 0.18 mmol) and NaCl (27 mg, 0.46 mmol) in DMF (0.61 mL) and H_2O (3 drops) heated to reflux for 2 d. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.32), compound ***epi*-12aa** was given as a colorless oil (10 mg, 16% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.39 (dd, *J* = 0.6, 1.8 Hz, 1 H), 7.23 - 7.18 (m, 2 H), 6.90 - 6.84 (m, 2 H), 6.33 (dd, *J* = 1.8, 3.1 Hz, 1 H), 6.19 (dd, *J* = 0.9, 3.4 Hz, 1 H), 3.80 (s, 3 H), 3.27 (tt, *J* = 3.5, 12.7 Hz, 1 H), 2.81 (ddd, *J* = 6.1, 13.7, 15.3 Hz, 1 H), 2.60 - 2.51 (m, 2 H), 2.26 - 2.18 (m, 1 H), 2.10 - 1.98 (m, 2 H), 1.69 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 210.9, 158.3, 157.2, 141.7, 127.7, 114.0, 109.9, 106.0, 55.3, 50.8, 45.2, 38.2, 37.6, 33.8, 22.1. **IR:** 2932 (w), 1709 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{18}H_{20}O_3$ 284.1412; Found 284.1404.

(2*S*,4*R*)/(2*R*,4*S*)-4-(4-Methoxyphenyl)-2-methyl-2-(thiophen-2-yl)cyclohexan-1-one (12ab): Prepared according to the general procedure using cyclohexenol **11ab** (76 mg, 0.21 mmol) and NaCl (37 mg, 0.64 mmol) in DMF (0.85 mL) and H_2O (3 drops) heated to reflux for 1.5 h. After work-up and purification, (10% EtOAc/Hexanes, R_f = 0.32), cyclohexanone **12ab** was given as a

colorless oil (33 mg, 52% yield). (*Diastereomeric ratio* = 4.3:1) **^{1}H NMR** (300MHz, $CDCl_3$) δ = 7.35 (dd, *J* = 2.9, 5.0 Hz, 0.37 H), 7.29 - 7.25 (m, 1 H), 7.22 - 7.15 (m, 2.37 H), 7.05 (dd, *J* = 1.5, 2.9 Hz, 0.25 H), 6.99 (dd, *J* = 3.5, 5.1 Hz, 1 H), 6.94 (dd, *J* = 1.5, 5.0 Hz, 0.31 H), 6.91 - 6.85 (m, 2.24 H), 6.77 (dd, *J* = 1.2, 3.5 Hz, 1 H), 3.81 (s, 3.56 H), 3.35 (tt, *J* = 3.4, 12.5 Hz, 1 H), 3.23 (tt, *J* = 3.2, 12.6 Hz, 0.24 H), 2.79 (dt, *J* = 6.2, 14.2 Hz, 1 H), 2.66 (td, *J* = 3.3, 14.2 Hz, 1.31 H), 2.51 - 2.41 (m, 1.13 H), 2.17 - 1.85 (m, 3.76 H), 1.40 (s, 3 H), 1.30 (s, 0.73 H). **^{13}C NMR** (75MHz, $CDCl_3$) δ = 210.9, 158.2, 148.7, 136.5, 127.6, 127.2, 124.1, 124.0, 114.0, 55.3, 51.9, 48.7, 38.9, 38.6, 34.4, 29.2. **IR:** 2926 (w), 1709 (s), 1611 (w), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{18}H_{20}O_2S$ 300.1184; Found 300.1175.

(2*S*,4*R*)/(2*R*,4*S*)-4-(4-Methoxyphenyl)-2-(5-methoxythiophen-2-yl)-2-methylcyclohexan-1-one (12ac): Prepared according to the general procedure using **11ac** (66 mg, 0.17 mmol) and NaCl (30 mg, 0.51 mmol) in DMF (0.68 mL) and H_2O (3 drops) heated to reflux for 21 h. After work-up and purification by prepTLC (15% EtOAc/Hexanes, R_f = 0.40), compound **12ac** was given as a yellow oil (21 mg, 37% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.20 - 7.15 (m, 2 H), 6.89 - 6.85 (m, 2 H), 6.36 (d, *J* = 3.7 Hz, 1 H), 6.04 (d, *J* = 3.7 Hz, 1 H), 3.88 (s, 3 H), 3.80 (s, 3 H), 3.36 (tt, *J* = 3.2, 12.6 Hz, 1 H), 2.85 (dt, *J* = 6.1, 14.2 Hz, 1 H), 2.50 (td, *J* = 3.3, 14.2 Hz, 1 H), 2.46 - 2.41 (m, 1 H), 2.15 - 2.07 (m, 1 H), 2.00 - 1.86 (m, 2 H), 1.36 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 210.9, 165.1, 158.2, 136.6, 134.4, 127.6, 121.3, 114.0, 103.3, 60.2, 55.3, 51.8, 48.3, 38.8, 38.5, 34.4, 28.8. **IR:** 2959 (w), 2926 (w), 1705 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{19}H_{22}O_3S$ 330.1290; Found 330.1286.

(2*R*,4*R*)/(2*S*,4*S*)-4-(4-Methoxyphenyl)-2-(5-methoxythiophen-2-yl)-2-methylcyclohexan-1-one (*epi*-12ac): Prepared according to the general procedure using **11ac** (66 mg, 0.17 mmol) and NaCl (30 mg, 0.51 mmol) in DMF (0.68 mL) and H_2O (3 drops) heated to reflux for 21 h. After

work-up and purification by prepTLC (15% EtOAc/Hexanes, R_f = 0.23), compound ***epi*-12ac** was given as a brown oil (18 mg, 33% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.22 - 7.17 (m, 2 H), 6.90 - 6.86 (m, 2 H), 6.51 (d, *J* = 4.0 Hz, 1 H), 6.04 (d, *J* = 4.0 Hz, 1 H), 3.86 (s, 3 H), 3.82 - 3.79 (m, 3 H), 3.26 (tt, *J* = 3.5, 12.5 Hz, 1 H), 2.82 (ddd, *J* = 6.4, 13.4, 15.3 Hz, 1 H), 2.60 - 2.53 (m, 1 H), 2.40 - 2.32 (m, 1 H), 2.28 - 2.17 (m, 2 H), 1.99 (dq, *J* = 5.0, 13.1 Hz, 1 H), 1.70 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 211.5, 165.5, 158.3, 136.5, 134.0, 127.7, 121.0, 114.0, 102.6, 60.1, 55.3, 51.4, 48.5, 38.1, 38.0, 33.6, 26.0. **IR:** 2934 (w), 1707 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{19}H_{22}O_3S$ 330.1290; Found 330.1291.

(2*R*,4*R*)/(2*S*,4*S*)-2-(2,5-Dimethylfuran-3-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (12ad): Prepared according to the general procedure using cyclohexenol **11ad** (107 mg, 0.29 mmol) and NaCl (51 mg, 0.87 mmol) in DMF (1.2 mL) and H_2O (3 drops) heated to reflux for 24 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.35), cyclohexanone **12ad** was given as a colorless oil (38 mg, 42% yield). *Only major diastereomer isolated.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.18 - 7.14 (m, 2 H), 6.89 - 6.85 (m, 2 H), 5.91 (d, *J* = 0.6 Hz, 1 H), 3.80 (s, 3 H), 3.22 (tt, *J* = 3.4, 12.5 Hz, 1 H), 2.75 (ddd, *J* = 6.1, 13.1, 14.0 Hz, 1 H), 2.48 (td, *J* = 3.2, 14.0 Hz, 1 H), 2.39 - 2.33 (m, 1 H), 2.26 (s, 3 H), 2.15 - 2.08 (m, 1 H), 2.07 (s, 3 H), 1.95 - 1.79 (m, 2 H), 1.21 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.5, 158.2, 149.6, 145.0, 136.7, 127.6, 122.0, 114.0, 105.2, 55.2, 48.3, 47.8, 39.0, 38.7, 35.8, 25.4, 13.5, 12.3. **IR:** 2963 (w), 2955 (w), 2928 (w), 1707 (s), 1512 (s) cm^{-1}. **HRMS (EI):** m/z: [M]+ Calcd. for $C_{20}H_{24}O_3$ 312.1725; Found 312.1719.

(2*R*,4*R*)/(2*S*,4*S*)-2-(2,5-Dimethylthiophen-3-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (12ae): Prepared according to the general procedure using cyclohexenol **11ae** (129 mg, 0.33 mmol) and NaCl (59 mg, 1.01 mmol) in DMF (1.3 mL) and H_2O (3 drops) heated to reflux for

18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.33), cyclohexanone **12ae** was given as a pale yellow oil (59 mg, 53% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.19 - 7.14 (m, 2 H), 6.90 - 6.85 (m, 2 H), 6.66 (d, *J* = 0.9 Hz, 1 H), 3.80 (s, 3 H), 3.26 (tt, *J* = 3.4, 12.5 Hz, 1 H), 2.76 (ddd, *J* = 6.0, 12.4, 14.0 Hz, 1 H), 2.67 (td, *J* = 3.3, 14.1 Hz, 1 H), 2.44 (s, 3 H), 2.41 - 2.34 (m, 1 H), 2.17 - 2.08 (m, 4 H), 1.95 - 1.83 (m, 2 H), 1.24 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 214.5, 158.2, 138.0, 136.5, 135.7, 131.5, 127.6, 124.8, 114.0, 55.2, 52.2, 48.8, 39.4, 38.7, 36.6, 24.8, 15.2, 13.7. **IR:** 2961 (w), 2926 (w), 2859 (w), 1707 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{20}H_{24}O_2S$ 328.1497; Found 328.1493.

(2*S*,4*R*)/(2*R*,4*S*)-2-(2,5-Dimethylthiophen-3-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (*epi*-12ae): Prepared according to the general procedure using cyclohexenol **11ae** (129 mg, 0.33 mmol) and NaCl (59 mg, 1.01 mmol) in DMF (1.3 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (10% EtOAc/Hexanes, R_f = 0.15), cyclohexanone ***epi*-12ae** was given as a pale yellow oil (20 mg, 18% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.20 - 7.16 (m, 2 H), 6.88 - 6.84 (m, 2 H), 6.56 (d, *J* = 0.9 Hz, 1 H), 3.79 (s, 3 H), 3.21 (tt, *J* = 3.5, 12.5 Hz, 1 H), 2.85 (ddd, *J* = 6.4, 13.7, 16.3 Hz, 1 H), 2.66 - 2.59 (m, 1 H), 2.37 (s, 3 H), 2.32 - 2.19 (m, 5 H), 2.12 - 1.99 (m, 2 H), 1.71 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 212.1, 158.2, 140.1, 136.7, 134.6, 131.3, 127.5, 125.5, 113.9, 55.3, 51.2, 48.2, 38.3, 37.9, 33.1, 25.4, 15.8, 15.1. **IR:** 2932 (w), 2924 (w), 2860 (w), 1705 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{20}H_{24}O_2S$ 328.1497; Found 328.1492.

(2*R*,4*R*)/(2*S*,4*S*)-2-(Benzo[*b*]thiophen-3-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (12af): Prepared according to the general procedure using **11af** (74 mg, 0.18 mmol) and NaCl (32 mg, 0.55 mmol) in DMF (0.74 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.68), compound **12af** was given as a colorless

oil (29 mg, 46% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.90 - 7.87 (m, 1 H), 7.73 - 7.70 (m, 1 H), 7.48 (s, 1 H), 7.37 - 7.31 (m, 2 H), 7.24 - 7.20 (m, 2 H), 6.92 - 6.88 (m, 2 H), 3.82 (s, 3 H), 3.58 (tt, *J* = 3.5, 12.6 Hz, 1 H), 2.90 (td, *J* = 3.4, 14.5 Hz, 1 H), 2.51 - 2.43 (m, 1 H), 2.38 - 2.32 (m, 1 H), 2.17 - 2.04 (m, 2 H), 2.01 - 1.90 (m, 1 H), 1.46 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 214.5, 158.3, 141.0, 137.2, 137.1, 136.2, 127.6, 124.4, 124.4, 123.0, 122.7, 122.1, 114.1, 55.3, 52.5, 48.3, 39.9, 38.3, 36.4, 25.2. **IR:** 2968 (w), 2930 (w), 1707 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{22}O_2S$ 350.1341; Found 350.1333.

(2*S*,4*R*)/(2*R*,4*S*)-2-(Benzo[*b*]thiophen-3-yl)-4-(4-methoxyphenyl)-2-methylcyclohexan-1-one (*epi*-12af): Prepared according to the general procedure using **11ae** (74 mg, 0.18 mmol) and NaCl (32 mg, 0.55 mmol) in DMF (0.74 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.32), compound ***epi*-12af** was given as a colorless oil (10 mg, 16% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.87 - 7.84 (m, 1 H), 7.46 (td, *J* = 0.9, 8.2 Hz, 1 H), 7.38 - 7.30 (m, 2 H), 7.24 (s, 1 H), 7.21 - 7.16 (m, 2 H), 6.86 - 6.82 (m, 2 H), 3.79 - 3.76 (m, 3 H), 3.37 (tt, *J* = 3.6, 12.6 Hz, 1 H), 3.02 (ddd, *J* = 6.3, 14.0, 16.1 Hz, 1 H), 2.77 - 2.71 (m, 1 H), 2.68 (t, *J* = 13.4 Hz, 1 H), 2.38 - 2.31 (m, 1 H), 2.30 - 2.19 (m, 1 H), 2.08 - 2.01 (m, 1 H), 1.89 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 211.9, 158.2, 136.7, 136.4, 127.6, 123.8, 123.8, 123.6, 123.3, 122.3, 113.9, 55.3, 47.0, 38.6, 38.2, 36.6, 33.5, 24.7, 24.4. **IR:** 2932 (w), 1703 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{22}H_{22}O_2S$ 350.1341; Found 350.1332.

(2*R*,4*R*)/(2*S*,4*S*)-4-(4-Methoxyphenyl)-2-methyl-2-(1-tosyl-1*H*-indol-3-yl)cyclohexan-1-one (12ag): Prepared according to the general procedure using **11ag** (145 mg, 0.27 mmol) and NaCl (47 mg, 0.80 mmol) in DMF (1.1 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.50), compound **12ag** was given as a pale

yellow oil (70 mg, 54% yield). *Major diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 8.03 - 8.00 (m, 1 H), 7.81 - 7.77 (m, 2 H), 7.58 (s, 1H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.32 (dt, *J* = 1.2, 7.8 Hz, 1 H), 7.25 (dd, *J* = 0.8, 9.0 Hz, 2 H), 7.23 - 7.16 (m, 3 H), 6.94 - 6.90 (m, 2 H), 3.83 (s, 3 H), 3.42 (tt, *J* = 3.4, 12.5 Hz, 1 H), 2.78 (td, *J* = 3.4, 14.0 Hz, 1 H), 2.47 - 2.39 (m, *J* = 5.6, 13.6 Hz, 1 H), 2.37 - 2.30 (m, 4 H), 2.13 - 2.00 (m, 2 H), 1.92 (dq, *J* = 4.1, 13.2 Hz, 1 H), 1.38 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 213.1, 158.4, 145.1, 136.1, 135.7, 135.0, 129.9, 128.8, 127.6, 126.8, 124.9, 124.6, 123.5, 122.9, 120.6, 114.1, 113.8, 55.3, 49.5, 47.2, 39.4, 38.5, 35.7, 25.6, 21.6. **IR:** 2930 (w), 1708 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{29}H_{29}O_4NS$ 487.1817; Found 487.1811.

(2*S*,4*R*)/(2*R*,4*S*)-4-(4-Methoxyphenyl)-2-methyl-2-(1-tosyl-1*H*-indol-3-yl)cyclohexan-1-one (*epi*-12ag): Prepared according to the general procedure using **11ag** (145 mg, 0.27 mmol) and NaCl (47 mg, 0.80 mmol) in DMF (1.1 mL) and H_2O (3 drops) heated to reflux for 18 h. After work-up and purification (20% EtOAc/Hexanes, R_f = 0.17), compound ***epi*-12ag** was given as a pale yellow oil (31 mg, 24% yield). *Minor diastereomer.* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.98 - 7.94 (m, 1 H), 7.77 - 7.72 (m, 2 H), 7.41 (s, 1H), 7.30 - 7.25 (m, 2 H), 7.24 - 7.16 (m, 5 H), 6.88 - 6.83 (m, 2 H), 3.78 (s, 3 H), 3.35 (tt, *J* = 3.4, 12.5 Hz, 1 H), 2.95 (ddd, *J* = 6.3, 14.0, 15.4 Hz, 1 H), 2.63 (ddd, *J* = 2.7, 4.6, 15.6 Hz, 1 H), 2.52 (t, *J* = 13.3 Hz, 1 H), 2.35 - 2.27 (m, 4 H), 2.17 - 2.03 (m, 2 H), 1.81 (s, 3 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 211.3, 158.3, 144.8, 136.2, 135.7, 135.3, 129.9, 128.9, 127.6, 127.1, 126.8, 124.3, 122.7, 122.7, 121.6, 114.0, 113.8, 55.3, 49.3, 47.2, 38.3, 38.0, 33.9, 23.6, 21.5. **IR:** 2931 (w), 1707 (s), 1514 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{29}H_{29}O_4NS$ 487.1817; Found 487.1814.

Allylation of 11aa. Synthesis of Methyl 1-allyl-3-(furan-2-yl)-5-(4-methoxyphenyl)-3-methyl-2-oxocyclohexane-1-carboxylate (13): Sodium hydride (33 mg as 60% dispersion in mineral oil, 0.83 mmol) was added to a flame-dried flask and cooled 0 ˚C. Cyclohexenol **11aa** (200 mg, 0.58 mmol) was dissolved in THF (1.2 mL) and added to the flask and stirred for 1 h at 0 ˚C. Allylbromide (0.10 mL, 1.20 mmol) was then added and the solution was warmed to room temperature and stirred overnight. The reaction mixture was quenched with sat. aq. NH_4Cl, extracted three times with EtOAc, dried over Na_2SO_4, and concentrated. The resulting crude mixture was purified by flash chromatography on silica gel (R_f = 0.30, 10% EtOAc/Hexanes) to give the desired compound as a colorless oil (118 mg, 53% yield). (*Diastereomeric Ratio = 7.1:3.6:3.1:1.0).* **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.41 (dd, *J* = 0.6, 1.8 Hz, 0.14 H), 7.38 (dd, *J* = 0.9, 1.8 Hz, 1.00 H), 7.37 (dd, *J* = 0.9, 1.8 Hz, 0.42 H), 7.35 (dd, *J* = 0.9, 1.8 Hz, 0.51 H), 7.29 (d, *J* = 8.9 Hz, 1.15 H), 7.27 - 7.24 (m, 1.38 H), 7.24 - 7.20 (m, 2.26 H), 6.92 - 6.86 (m, 4.45 H), 6.39 (dd, *J* = 1.8, 3.4 Hz, 1.01 H), 6.33 (dd, *J* = 1.8, 3.4 Hz, 0.58 H), 6.31 (dd, *J* = 1.8, 3.1 Hz, 0.56 H), 6.29 - 6.27 (m, 0.43 H), 6.24 (dd, *J* = 0.9, 3.4 Hz, 1.02 H), 6.18 (dd, *J* = 0.8, 3.2 Hz, 0.66 H), 5.68 - 5.51 (m, 2.20 H), 5.09 - 4.93 (m, 4.50 H), 3.89 - 3.82 (m, 0.66 H), 3.82 - 3.80 (m, 6.14 H), 3.80 (s, 0.48 H), 3.76 (s, 3.09 H), 3.75 (s, 0.41 H), 3.54 - 3.47 (m, 0.15 H), 3.44 (s, 1.64 H), 3.43 - 3.35 (m, 1.09 H), 3.34 (s, 1.30 H), 2.97 - 2.75 (m, 2.91 H), 2.68 - 2.63 (m, 1.41 H), 2.63 - 2.57 (m, 1.86 H), 2.55 - 2.46 (m, 1.69 H), 2.39 - 2.33 (m, 0.49 H), 2.16 (td, *J* = 3.4, 13.9 Hz, 1.10 H), 2.12 - 1.93 (m, 3.92 H), 1.78 - 1.72 (m, 0.22 H), 1.60 (s, 0.35 H), 1.55 (s, 1.67 H), 1.43 (s, 1.44 H), 1.42 (s, 2.96 H). **^{13}C NMR** (126MHz, $CDCl_3$) δ = 207.0, 206.8, 205.6, 204.1, 172.1, 171.7, 171.3, 170.2, 158.4, 158.3, 158.3, 157.3, 156.2, 156.0, 155.1, 142.2, 142.0, 141.8, 141.8, 137.1, 136.4, 136.2, 136.2, 133.1, 132.7, 132.6, 127.8, 127.8, 127.7, 127.6, 119.2, 119.1, 119.0, 119.0, 114.0, 114.0, 114.0, 114.0, 113.8, 110.7, 110.5, 110.3, 109.9, 107.1, 106.0, 106.0,

105.3, 61.7, 59.1, 58.9, 58.8, 55.3, 52.6, 52.4, 52.3, 52.0, 50.9, 49.7, 49.6, 45.0, 44.3, 44.2, 42.2, 41.6, 41.6, 41.2, 41.1, 40.6, 39.1, 38.5, 36.9, 34.9, 34.8, 34.2, 33.7, 29.7, 27.0, 26.1, 24.3, 22.2. **IR:** 2951 (w), 2932 (w), 1736 (m), 1711 (s), 1512 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{23}H_{26}O_5$ 382.1780; Found 382.1777.

Procedure for Intramolecular [4+2] Cycloaddition. Compound **13** (59 mg, 0.15 mmol) was dissolved in xylenes (3.1 mL) and heated to reflux for 24 h. The reaction mixture was concentrated and purified by prep-TLC (R_f = 0.04, 10% EtOAc/Hexanes) to give cycloadduct **14** (15 mg, 46% yield based on 32.4 mg of reacting *syn*-diastereomers of **13**). Starting material **13** was also recovered (27 mg, 46% recovery). (*Diasteromeric ratio = 5.3:1*) **^{1}H NMR** (500MHz, $CDCl_3$) δ = 7.21 - 7.17 (m, 2.14 H), 7.17 - 7.13 (m, 0.57 H), 6.89 - 6.85 (m, 2.13 H), 6.85 - 6.82 (m, 0.38 H), 6.45 (dd, *J* = 1.5, 5.8 Hz, 0.98 H), 6.39 (d, *J* = 6.1 Hz, 0.99 H), 5.00 (dd, *J* = 1.7, 4.7 Hz, 0.99 H), 4.27 - 4.25 (m, 0.18 H), 3.80 (s, 3.18 H), 3.78 (s, 0.60 H), 3.75 (s, 2.94 H), 3.74 (s, 0.53 H), 3.66 (tt, *J* = 5.1, 13.4 Hz, 1.19 H), 2.85 - 2.78 (m, 1.14 H), 2.78 - 2.73 (m, 0.18 H), 2.72 - 2.61 (m, 0.43 H), 2.53 - 2.38 (m, 4.50 H), 2.36 - 2.30 (m, 1.84 H), 2.06 (t, *J* = 14.0 Hz, 1.31 H), 1.93 - 1.86 (m, 0.42 H), 1.75 (dd, *J* = 6.9, 11.4 Hz, 1.11 H), 1.63 - 1.56 (m, 1.70 H), 1.53 - 1.47 (m, 0.28 H), 1.40 - 1.35 (m, 0.23 H), 1.22 (s, 0.57 H), 1.11 (s, 3.00 H). **^{13}C NMR** (126MHz ,$CDCl_3$) δ = 211.6, 210.9, 172.4, 172.3, 158.5, 158.4, 140.2, 138.0, 137.7, 135.8, 135.6, 133.0, 129.9, 128.3, 127.8, 127.8, 127.4, 126.8, 126.0, 114.1, 114.0, 99.9, 97.7, 94.7, 79.1, 78.5, 58.7, 58.3, 55.3, 55.3, 52.4, 52.3, 50.0, 49.2, 47.3, 47.1, 45.2, 43.8, 43.5, 41.3, 40.8, 40.7, 40.6, 39.8, 37.9, 37.3, 37.2, 36.7, 34.4, 21.4, 19.0, 17.0. **IR:** 2949 (w), 1734 (s), 1717 (s), 1610 (w), 1512 (s) cm^{-1}. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{23}H_{26}O_5$ 383.1853; Found 383.1854.

ASSOCIATED CONTENT

Supporting Information

Optimization tables for the reaction of cyclopropane **5a** and anisole (**6a**). ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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